Physical Chemistry

FOR

PREMEDICAL STUDENTS

INTERNATIONAL CHEMICAL SERIES

Louis P. Hammett, Ph.D., *Consulting Editor*

Physical Chemistry
FOR
PREMEDICAL STUDENTS

BY

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INTERNATIONAL STUDENT EDITION

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PHYSICAL CHEMISTRY FOR PREMEDICAL STUDENTS

INTERNATIONAL STUDENT EDITION

PREFACE TO THE SECOND EDITION

Experience in the use of the first edition has indicated ways in which the book may be made more useful to the student. With two exceptions these have not involved any major change in the plan of the text. However, the number of minor changes is such that many portions of the book have been completely rewritten.

In some cases material has been omitted when its value to the student did not seem to justify its retention. In other cases new material has been added and old material has been revised and expanded. In all cases the attempt has been made to approach each topic from the student's standpoint, with the objective of making the subject matter increasingly intelligible to him without sacrifice of accuracy.

The first major change is in the discussion of protolytic equilibrium. This is treated in a manner which it is hoped will prove less cumbersome than the conventional approach as it decreases appreciably the number of separate equations to be learned by the student.

The second major change is the introduction of a chapter on thermodynamics. The author believes that the advantages of even the most elementary knowledge of this subject are such as to justify its inclusion in this text. The chapter introduces the terms energy, heat content, reversible process, entropy, and free energy. It shows the relation between free-energy changes, electrode potentials, and equilibrium constants. Simple illustrative problems are worked out, and the mathematics of the discussion is kept as simple as possible.

Some of the changes have necessitated the use of equations whose derivation is beyond the scope of the book. However, every effort has been made to point out the significance and the limitations of these equations so that the student can use them intelligently.

The conventions concerning the sign of electrode potentials have been changed to conform to those employed by the majority of writers on physical chemistry.

The author acknowledges gratefully his indebtedness to his colleagues, Professors Andrew J. Scarlett and John H. Wolfenden, who read the entire manuscript and made many helpful suggestions; to Dr. William E. Cadbury, Jr., of Haverford College, for his careful and detailed criticism of the first edition; and to Dr. Louis P. Hammett for his encouragement and counsel during the preparation of the present edition. The author alone is responsible for any errors that may be found in the text and will appreciate having them brought to his attention.

<div style="text-align: right">JOHN PAGE AMSDEN</div>

HANOVER, N.H.
May, 1950

PREFACE TO THE FIRST EDITION

One of the important factors making possible the tremendous advances in medical practice during the last century has been the application of chemistry to the understanding and control of the reactions taking place in the human body. This is evidenced by countless examples, from the work of Pasteur and his predecessors down to the present time. In recent years, the application of the principles of physical chemistry has been of great value in forwarding the work of the physician. An elementary knowledge of this particular branch of chemistry is almost essential for anyone who would understand what is being done at present or would engage in the search for new methods for the control of disease.

A course in physical chemistry belongs in the program of the premedical student. This program, however, is already so full of required courses that the work in physical chemistry should be as brief as is consistent with an adequate presentation of the elementary principles of the subject. The material contained in this text has been chosen with that objective in mind. It does not pretend to cover the whole field of physical chemistry but contains those phases of the subject that appear to be of value to the general medical student. Students intending to do research in biological fields will find it advisable to take at least a year's work in physical chemistry, using one of the more comprehensive texts. The material here presented may be covered in one semester and should enable the student to read, understand, and apply much of the work that is being reported in the current literature and to have a better comprehension of the reactions taking place in the human body.

The author has always felt that for the student to appreciate fully the possibilities and limitations of the equations of physical chemistry it is essential that he be familiar with their derivation. For this reason, the derivations of the equations used are included in the text. In a few cases, these derivations have required the use of calculus. Except in these cases the mathematical demands

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are limited to an ability to solve quadratic equations and to use logarithms.

When material is presented as a lecture course, it is found that demonstrations are one of the most forceful means of implanting facts or ideas in the student's mind. An effort has been made to describe many such demonstrations, which are simple to perform and yet serve to illustrate the points discussed. In many cases, the application of the principles discussed to medical work has been suggested.

Since physical chemistry is valuable only as it can be used to solve problems in practice and in research, it is necessary that the student gain as much practice as time permits in the application of principles to the solution of problems. For this reason, many problems have been included at the end of each chapter. An effort has been made to start off with simple exercises in order that the student may gain confidence in his ability to solve problems; then the complexity of the problems has been increased. At the same time the attempt has been made to devise problems that are not merely mathematical exercises but involve some reasoning on the part of the student.

JOHN PAGE AMSDEN

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TO THE STUDENT

Physical chemistry may be defined as the study of the laws governing the physical and chemical conduct of substances. As a result of experiment, it is able to make general statements as to *how* substances behave. It then proceeds, as far as possible, to explain *why* they behave in this way. Within limitations, a knowledge of physical chemistry makes possible a prediction of what will happen under a given set of conditions and, to a certain extent, the control of the course of the reaction.

Physical chemistry should be considered as a set of tools—an extremely useful set, but one that attains its greatest value only in the hands of a person who is familiar with it, who knows which tool to select for a given task and how to use it. This text attempts to help the student to acquire that ability by first describing each tool and how it is made, then showing, by examples, what kind of job each tool will do and how to use it, and finally, by means of problems, giving him a chance to use the tools himself and to become familiar with their application.

The number of formulas and equations found in the text appears disconcerting at first glance, but closer examination will reveal that the most advanced mathematics required is an ability to solve quadratic equations. However, the ability to use logarithms is essential, and the possession of and ability to use a slide rule will be a great help. In the derivation of a few of the equations, the use of the calculus has been unavoidable. The student unfamiliar with the calculus will have to take the results on faith.

CHAPTER 1

DIMENSIONS AND UNITS

In Lewis Carroll's classic, "Through the Looking Glass," Humpty Dumpty is quoted as saying to Alice, "When *I* use a word it means just what I choose it to mean—neither more nor less." In the discussions of physical chemistry the meanings assigned to the words used are not so unorthodox as those chosen by Humpty Dumpty. Nevertheless, many of the terms to be employed do have a precise meaning, and it is important that they should convey the same meaning—neither more nor less—to the author and to the reader. In order to make sure of this mutual understanding, this first chapter is devoted to defining certain words that will be used frequently in the succeeding work.

In the study of physical chemistry it is constantly necessary to describe substances by means of their properties or to define their state or condition. The purpose of this description is to convey to someone else an accurate picture of the object under discussion. To accomplish this description, three things are necessary: the *numerical value* of the property, the *dimensions* of the property, and the *units* in which the value is expressed. In order that the picture conveyed shall be clear and accurate, these dimensions and units must mean the same thing to all parties to the discussion. For instance, suppose that an attempt is being made to describe an individual and the statement is made that he is six. If this value refers to age, it conveys a quite different picture of the person than if it refers to height. Therefore the dimension, either time or length, of the property must be stated. Suppose that it does refer to age; the picture again is quite different if the age is six months or six years. For this reason, the units in which the value is expressed must be included. The statement that the individual is six months old helps us to visualize him correctly.

To return to examples more pertinent to physical chemistry,

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the density of mercury is one of its properties.   The value of this property is 13.6, but this statement is meaningless unless it is also known that density has the dimensions of mass divided by volume and that the units in which these dimensions are expressed are grams per cubic centimeter.   The statement that the density of mercury is 13.6 g./cm.^{3} is perfectly definite and should convey the same meaning to all who read it.

Again, the condition of a body may be described by saying that it has a velocity of 57, but in order for this statement to be significant, it must also be known that velocity has the dimensions of length divided by time and that the units in which this particular velocity is expressed are centimeters per second.

A knowledge of the dimensions and units used in stating the properties and conditions of substances is essential for understanding the work of physical chemistry.

Fundamental Dimensions and Their Units

There is a wide variety of terms used in describing substances or in defining their condition, but it is found, upon examination, that they are all expressible in terms of four fundamental dimensions: *length, mass, time*, and *temperature*.   Each of these dimensions has had a definite unit assigned to it for scientific work. In the metric system, which is in almost universal use, these units are the *centimeter*, the *gram*, the *second*, and the *degree centigrade*.   From the first three units, the system gets its common name of the *centimeter-gram-second*, or *c.g.s.*, system. In establishing reference standards for each of these units, an attempt was made to relate them to certain natural constants. That this attempt was not wholly successful will be shown in the discussion of the various units.   This failure resulted from the inaccuracies of the methods of measurement at the time the units were established.

Length.   The standard of length is the *meter* (m.) which is defined as the distance, at 0°C., between two lines on a platinum bar that is kept at the International Bureau of Weights and Measures in Sèvres, France.   This standard is known as the International Prototype Meter. Originally the meter was intended to be 1/10,000,000 of the distance on the earth's surface from the equator to the north pole, measured along a meridian of longitude.   It has since been shown that this distance

is about 10,000,856 m., but the length of the standard meter remains unchanged. The unit of length in the c.g.s. system is the *centimeter* (cm.), which is 0.01 m.

$$1 \text{ m.} = 100 \text{ cm.} = 39.37 \text{ in.}$$
$$1 \text{ cm.} = 10 \text{ millimeters (mm.)} = 0.3937 \text{ in.}$$
$$1 \text{ in.} = 2.54 \text{ cm.}$$

Mass. The standard of mass is the *kilogram* (kg.), which is defined as the mass of a block of platinum, also kept at the International Bureau of Weights and Measures. This block of platinum is known as the International Prototype Kilogram and was supposed to have a mass equal to that of 1,000 cm.³ of pure water under a pressure of 1 atmosphere (atm.) and at a temperature of 3.98°C., this being the temperature at which water has its maximum density. It has since been shown that this volume of water, under the stated conditions, has a mass of only 0.999972 kg., but the mass of the standard kilogram remains unchanged. The unit of mass used in the c.g.s. system is the *gram* (g.), which is 0.001 kg.

$$1 \text{ kg.} = 1,000 \text{ g.} = 2.20 \text{ lb. (avoirdupois)}$$
$$1 \text{ g.} = 0.035 \text{ oz. (avoirdupois)}$$
$$1 \text{ oz. (avoirdupois)} = 28.35 \text{ g.}$$

The difference between *mass* and *weight* should be noted. Mass may be defined as that which has the property of inertia, or resistance to any change in its state of motion, and is constant. Weight, however, as we know it, is the result of the action of gravity on a mass, and since the force of gravity varies somewhat in different parts of the earth's surface, a given mass may have a variety of weights depending upon its location.

Time. The standard of time is the *mean solar day,* or the average length of time, throughout the year, between two successive crossings of the meridian by the sun. The unit of time in the metric system is the *second* (sec.), which is 1/86,400 of a mean solar day.

Temperature. Temperatures are expressed in *degrees* (°). Of the various temperature scales that have been devised, only three are in common use at the present time. These are the *Fahrenheit,* the *centigrade.* and the *absolute,* or *Kelvin,* scales. The first is in

general household use in the United States, and the last two are in almost universal use in scientific work throughout the world.

The Fahrenheit Scale (°F.).   The first of these temperature scales was developed by the German physicist Fahrenheit, in 1714.   He chose as the zero point for his scale the temperature of a mixture of ice, water, and salt, believing that this was the lowest temperature that could be obtained conveniently.   For the other point on the scale, he chose the temperature of the normal human body, measured at the armpit, and called this 12°. This, however, produced a degree that was inconveniently large, so later each degree was subdivided into 8 degrees and the temperature of the body was called 96°.

The present reference points for the Fahrenheit scale are the freezing and boiling points of pure water under certain specified conditions.   These two temperatures are constant and reproducible, which cannot be said of the two originally selected by Fahrenheit.   On this revised scale the freezing point of pure water, *i.e.*, the temperature at which water, in contact with air at 1 atm., is in equilibrium with ice, is assigned the value 32°F.; the boiling point of pure water, *i.e.*, the temperature at which water is in equilibrium with water vapor at a pressure of 1 atm., is assigned the value 212°F.   Therefore, the degree Fahrenheit (°F.) is $\frac{1}{180}$ of the temperature difference between the freezing and boiling points of pure water under a pressure of 1 atm.

The Centigrade Scale (°C.).   The centigrade scale uses the same two reference points (the freezing and boiling points of water) as does the Fahrenheit scale but calls the freezing point 0° and the boiling point 100°.   Therefore, the degree centigrade (°C.) is $\frac{1}{100}$ of this temperature difference.   From this it will be seen that the degree centigrade is $\frac{9}{5}$ as large as the degree Fahrenheit.   In equations, centigrade temperatures are usually indicated by *t*.

The Absolute, or Kelvin, Scale (°A. or °K.).   This scale is sometimes called after Lord Kelvin, the Scottish physicist who first proposed it.   The theoretical significance of the scale will be considered in the chapter on gases.   It will suffice for the present to note that the 0° on this scale is the *absolute zero*, or lowest possible temperature.   This is equal to −273.16°C.   (In this text we shall use the approximate value −273°C.)   The size of the degree absolute is the same as that of the degree centigrade.   In

equations, absolute temperatures are usually indicated by T. In practically all the calculations in physical chemistry, temperatures must be expressed on the absolute scale.

The relation between these three temperature scales may be summarized as follows:

Size of the degree
$$°K. = °C. = \tfrac{9}{5}°F.$$

To change from one scale to another:

Fahrenheit to centigrade
$$t \text{ in } °C. = \tfrac{5}{9}(t \text{ in } °F. - 32)$$

Centigrade to absolute
$$T \text{ in } °K. = t \text{ in } °C. + 273$$

Example. What temperature, in degrees centigrade and degrees Kelvin, corresponds to 68°F.?

$$\tfrac{5}{9}(68 - 32) = 20°C. = 293°K.$$

TABLE 1-1. RELATION BETWEEN THE THREE TEMPERATURE SCALES

°F.	°C.	°K.
−459.4	−273	0
0	− 17.8	255.2
32	0	273
68	20	293
212	100	373

DIMENSIONS AND UNITS OF OTHER PROPERTIES

From the four fundamental dimensions—length, mass, time, and temperature—may be derived all the other means of describing substances or defining their state. The more common of these properties, with their dimensions and units, follow.

Area. Area is the square of a length. Its unit is the *square centimeter* (cm.²).

Volume. Volume is the cube of a length. Its unit is the *cubic centimeter* (cm.³).*

Density. Density is mass per unit volume. Its unit is the *gram per cubic centimeter* (g./cm.³). From what was said under

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* It will avoid confusion in later work if the student will always write cm.² and cm.³ instead of sq. cm. and cc.

the discussion of mass, it is apparent that the density of pure water, at its maximum, was intended to be 1.0 g./cm.³ Actually, the value is 0.999972 g./cm.³

Specific Gravity. The specific gravity of a substance is equal to the density of that substance divided by the density of some specified reference substance. For solids and liquids, the most common reference substance is water. For gases, the reference substances are either air or hydrogen. When no standard is specified, it is assumed to be water. When no temperature is specified, it is assumed that substance and standard are at the same temperature, usually 20°C. When specific gravity is given by the expression 5.6$\frac{15°}{4}$, it means that the specific gravity of the substance, at 15°C., is 5.6 referred to water at 4°C.

Specific gravity has no dimensions. Specific gravity is numerically equal to density, when the latter is expressed in c.g.s. units, and when the reference standard is water.

Velocity. Velocity is length traversed per unit time. The unit of velocity is the *centimeter per second* (cm./sec.). The usual symbol for velocity is *c*.

Acceleration. Acceleration is defined as change in velocity per unit time. Its unit is the *centimeter per second per second* (cm./sec.²). For freely falling objects under the influence of gravity, the average acceleration is 980.7 cm./sec.² That is, during every second that they fall, their velocity increases by 980.7 cm./sec. The symbol for the acceleration of gravity is *g*.

Force. Force is that which is capable of producing an acceleration of a mass. Force is, therefore, equal to mass multiplied by acceleration. The unit of force is the *dyne*. The dyne is defined as the force which, acting upon a mass of 1 g. for 1 sec., will change its velocity by 1 cm./sec. (dynes = g. × cm./sec.²).

As stated above, the acceleration produced by gravity is nearly constant and is equal to 980.7 cm./sec.² From this it follows that the force of gravity is nearly constant and that the force exerted by gravity on a mass of 1 g. is equal to 980.7 dynes. In other words, if a mass of 1 g., under the influence of gravity, is resting on a surface, it is pressing down on that surface with a force of 980.7 dynes.

It will be recalled that weight is the result of the action of gravity on a mass. In other words, weight is the force exerted by gravity on a mass. From this it follows that weight should be

expressed in force units, *i.e.*, in dynes. The average weight of a mass of 1 g. is 980.7 dynes. Unfortunately, it is the common but confusing practice to express this weight in grams rather than in dynes, it being tacitly understood that 1 g. of weight equals 980.7 dynes. It should be noted that whereas 1 g. of mass is a constant, 1 g. of weight is variable, depending on the value of the force of gravity in the locality of the measurement.

In this work we shall reserve the term *gram* for the unit of mass and shall use the term *gram-weight* (g.-wt.) for the unit of weight.

Pressure. Pressure is defined as force per unit area on a surface. The unit of pressure is the *dyne per square centimeter* (dyne/cm.²). Pressure may also be expressed as weight per unit area on a surface. In this case the unit is the *gram-weight per square centimeter* (g.-wt./cm.²). From what was said in the discussion of force, it is apparent that

$$1 \text{ g.-wt./cm.}^2 = 980.7 \text{ dynes/cm.}^2$$

Work or Energy. When a force acts through a certain distance, energy is transformed or work is done. These two concepts, work and energy, are different aspects of the same thing. They have the same dimensions and are expressed in the same units. Work is equal to force multiplied by distance. In absolute units, work is expressed in *ergs*. The erg is defined as the work done when a force of 1 dyne acts through a distance of 1 cm. (ergs = dynes × cm.).

Work may also be expressed in terms of *grams-weight times centimeters*.

$$1 \text{ g.-wt.} \times \text{cm.} = 980.7 \text{ ergs}$$

The erg is at times inconveniently small to use in calculations. Therefore, the *joule* is often used in its place.

$$1 \text{ absolute joule} = 10,000,000 \text{ ergs} = 1 \times 10^7 \text{ ergs}$$

In the working out of problems in which both pressure and work are involved, care must be taken to express both of these properties in consistent units. If the pressure is stated in dynes per square centimeter, work must be given in ergs. If, on the other hand, pressure is given in grams-weight per square centimeter, work must be expressed in grams-weight times

centimeters. Failure to observe this rule will result in most peculiar answers.

Heat. The standard quantity of heat is that amount which is necessary to raise the temperature of 1 g. of water 1°C. This unit of heat is known as the *small calorie* (cal.). The value of the calorie depends upon the temperature at which it is measured.

The 15° *calorie* is the amount of heat required to raise the temperature of 1 g. of water from 14.5°C. to 15.5°C.

The *mean calorie* is $\frac{1}{100}$ of the amount of heat necessary to raise the temperature of 1 g. of water from 0°C. to 100°C.

The value of the 15° calorie differs slightly from the value of the mean calorie, but for all ordinary work they may be considered the same.

The *large calorie* (Cal.), or *kilogram-calorie* (kg.-cal.), is equal to 1,000 cal.

It is common experience that work can be transformed into heat, as when the hand is rubbed briskly over a smooth surface, and also that heat may sometimes be transformed into work, as in the steam engine. Apparently, then, heat is one form of energy and should be expressible in the same units and dimensions. The relation between the calorie and the other units (ergs and joules) in which energy is expressed was based on the assumption that it was possible to determine accurately the amount of energy required to raise the temperature of 1 g. of water 1°C. Each improvement in the technique of making this measurement has resulted in a change in the value of the calorie in joules. To avoid a continuance of these changes Rossini[1] suggested that there be established an arbitrary value for the calorie, not directly related to the heat capacity of water. This *defined calorie*, or *thermochemical calorie*, has been generally accepted by thermochemists. It has the following values:

1 cal. (defined) = 42,660 g.-wt. × cm. = 4.1840 × 10⁷ ergs
1 cal. (defined) = 4.1840 absolute joules
1 cal. (defined) = 4.1833 international joules

The distinction between the *international joule* and the *absolute joule* (as previously defined in the section on work or energy) will be discussed in the section on electrical units.

[1] BICHOWSKY, F. R., and F. D. ROSSINI, "Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, 1936.

The value of the defined calorie happens to correspond to the present accepted value of the specific heat capacity of water at 17°C. but it is not defined in terms of that heat capacity.

Heat Capacity. The *heat capacity* of a system is the number of calories required to raise the temperature of the system 1°C. The *specific heat capacity* (or, simply, *specific heat*) of a substance is the number of calories required to raise the temperature of 1 g. of the substance 1°C. The specific heat of water is very close to 1 cal./(g. $\times$ °C.). Almost all other substances have a specific heat less than that of water.

AUXILIARY UNITS

At times it is more convenient to use other units of pressure, mass, and volume than those already discussed. The more important of these auxiliary units follow.

Pressure. Pressure may be expressed in *atmospheres* (atm.) or in *centimeters of mercury* (cm. of Hg). The atmosphere is the pressure just sufficient to support, at 0°C., in a barometer tube, a column of mercury 76.00 cm. high.

$$1.000 \text{ atm.} = 76.00 \text{ cm. of Hg}$$
$$1.000 \text{ atm.} = 1.033 \times 10^3 \text{ g.-wt./cm.}^2$$
$$1.000 \text{ atm.} = 1.013 \times 10^6 \text{ dynes/cm.}^2$$

Mass. The mass of any substance is often expressed in *moles* (sometimes called *gram-molecules*). One mole is that amount of the substance whose mass in grams is numerically equal to the molecular weight of the substance. For example, the molecular weight of oxygen is 32.0000; therefore one mole of oxygen is 32.0000 g. of that substance. The important fact concerning this unit is that one mole of any one substance contains the same number of individual molecules as does one mole of any other substance. This number of molecules per mole has been shown to be 6.02×10^{23} and is known as *Avogadro's number*. The symbol for number of moles is n or N.

A similar unit is the *gram-atom* of an element. This is the mass in grams of that element numerically equal to its atomic weight. The gram-atom of oxygen is 16.0000 g. The gram-atoms of all elements contain the same number (6.02×10^{23}) of individual atoms.

Volume. Volume is often expressed in *liters*. One liter is so nearly equal to 1,000 cm.³ that they may be considered identical

for all practical purposes. Actually the liter is that volume of water which has a mass of 1,000 g. at 1 atm. pressure and 3.98°C. This volume is 1,000.028 cm.³

Vessels for use in volumetric measurements are usually graduated in *milliliters* (ml.) rather than in cubic centimeters. For all practical purposes, however, the difference is negligible.

$$1 \text{ liter} = 1,000 \text{ ml.}$$
$$1 \text{ liter} = 1,000.028 \text{ cm.}^3$$
$$1 \text{ liter} = 1.06 \text{ quarts}$$
$$1 \text{ ml.} = 1.000028 \text{ cm.}^3$$

Electrical Properties and Their Units

A separate set of units is used in describing the electrical properties of matter. These units may be expressed in terms of the fundamental dimensions of length, mass, and time, but there must also be used two terms whose dimensions are not known, *viz.*, the dielectric constant and the magnetic permeability of the medium in which the measurement of the properties is carried on. The resulting expressions are fairly complex, and their use in this text does not seem justified. Therefore, in the following discussion, only the common definitions of the electrical units will be given and their relation to each other shown.

It will be recalled that when the International Prototype Kilogram was established as the reference standard for mass it was intended that it should be exactly equal to the mass of 1,000 cm.³ of pure water, at 1 atm. and 3.98°C. Subsequent refinements of the technique of measurement showed that this was not so, but that 1,000 cm.³ of water had a mass slightly less than 1 kg. By international agreement, however, our reference standard for mass is the arbitrarily established kilogram, rather than the mass of a particular volume of water. A similar situation exists with respect to electrical units. These units were originally defined in terms of the c.g.s. system. The units so defined are known as *absolute units*. Later, for purposes of convenience, certain reference standards for these units were established. It was intended that there should be an exact correspondence between the values assigned to these reference standards and the absolute units. However, later refinements of the technique of measurement disclosed discrepancies between these assigned values and the abso-

lute units. By international agreement we have retained these arbitrarily established standards as our reference standards. The electrical units defined in terms of these standards are known as *international units* and differ slightly in value from the absolute units. These differences will be pointed out when the various units are discussed.

Quantity of Electricity. As far as we know, the smallest quantity of electricity is the charge on the *electron*. The electron is a tiny particle whose mass is about 1/1,850 that of the hydrogen atom. It bears a negative charge. Electrons can be obtained isolated from any other form of matter, as, for example, in the cathode tube. The charge on the electron may be considered as the ultimate unit, or atom, of electricity. The symbol for the electron is e.

Up to 1932, no similar particle bearing a positive charge had been found. The smallest amount of matter which had been found associated with positive electricity was the hydrogen ion, H^+, sometimes called the *proton*. The proton has a mass almost equal to that of the hydrogen atom and bears a charge equal and opposite to that of the electron. When a hydrogen atom loses one electron, what is left is the proton.

$$H \rightarrow H^+ + e$$

In 1932, at the California Institute of Technology, evidence was obtained of the existence of a particle having the same mass as an electron and bearing a charge equal in amount, but opposite in sign, to that on the electron. This particle, bearing a unit charge of positive electricity, has been named the *positron*.

Electrostatic Unit of Electricity. Before anything was known about electrons, protons, and positrons, a unit quantity of electricity had been defined. This unit, the *electrostatic unit* (e.s.u.), is still used as the standard quantity of electricity. The electrostatic unit is defined as that quantity of electricity which, if placed in a vacuum 1 cm. distant from an equal and similarly charged quantity, will repel it with a force of 1 dyne.

$$1 \text{ e.s.u. of quantity} = 2.08 \times 10^9 \text{ } e$$

Coulomb. The electrostatic unit is too small for use as a practical unit of quantity of electricity. The unit commonly used is the *coulomb*, which is equal to 3.00×10^9 e.s.u. of quantity.

This coulomb, since it is based upon the electrostatic unit which was defined in terms of the c.g.s. system, is known as the *absolute coulomb*.

1 absolute coulomb $= 3.00 \times 10^9$ e.s.u. of quantity
$$= 6.24 \times 10^{18} e$$

The reference standard for the coulomb is that quantity of electricity which will deposit, under certain specified conditions, 0.001118 g. of metallic silver from a solution of silver nitrate. The coulomb so defined is known as the *international coulomb*.

1 international coulomb $= 0.999835$ absolute coulomb

Faraday. When hydrogen gas is changed to hydrogen ion, there is released from each hydrogen atom one electron. From all the atoms in 1 gram-atom of hydrogen, there will be released 6.02×10^{23} electrons. This quantity of electricity is known as the *faraday* (*F*).

1 faraday $= 96,496$ absolute coulombs
$$= 96,512 \text{ international coulombs}$$

It will be noticed that the faraday contains the same number of electrons as there are molecules in a mole. For this reason the faraday may be considered as 1 mole of electricity. In this text we shall use the approximate value of 96,500 coulombs for the faraday.

Electrical Current. Electrical current is pictured as a flow of electrons through a conductor from a region of high electron pressure to one of low electron pressure. The current strength is the rate of flow measured in coulombs per second. A current of 1 coulomb/sec. is said to have a strength of 1 *ampere* (amp.).

$$\text{Amperes} = \frac{\text{coulombs}}{\text{second}}$$

1 international amp. $= 0.999835$ absolute amp.

Potential Difference. The difference in pressure of electrons at the two ends of a conductor causing them to flow through the conductor is called the *potential difference*. This potential difference is measured in *volts*.

The electrostatic unit of potential difference exists between

two points if the transfer of 1 e.s.u. of quantity of electricity between them requires the expenditure of 1 erg of energy.

$$1 \text{ absolute volt} = \tfrac{1}{300} \text{ e.s.u. of potential difference}$$

The reference standard for potential difference is that existing between the poles of the Weston normal cell at 20°C. By international agreement this has been assigned the value 1.0183 international volts. Therefore, 1 international volt is 1/1.0183 of the voltage of the Weston normal cell at 20°C.

$$1 \text{ international volt} = 1.000330 \text{ absolute volts}$$

Resistance. All conductors offer a resistance to the flow of electrons through them. This is comparable to the frictional resistance that a pipe offers to a liquid flowing through it. Electrical resistance is measured in *ohms*. One *absolute ohm* is the resistance such that a potential difference of 1 absolute volt will drive a current of 1 absolute ampere through it.

$$\text{Ohms} = \frac{\text{volts}}{\text{ampere}}$$

The reference standard for resistance is that offered, at 0°C., by a column of mercury of constant cross section, having a mass of 14.4521 g. and a length of 106.3 cm. at that temperature. The resistance of this column is 1 *international ohm*.

$$1 \text{ international ohm} = 1.000495 \text{ absolute ohms}$$

Electrical Work. When a current flows through a conductor, work is done. This work is equal to the amount of electricity that flows multiplied by the potential difference that is causing it to flow. Since this product represents work, it must be expressible in any of the work units. The values of the volt and the coulomb have been so chosen that

$$\text{Volts} \times \text{coulombs} = \text{joules}$$
$$\text{Absolute volts} \times \text{absolute coulombs} = \text{absolute joules}$$
$$\text{International volts} \times \text{international coulombs}$$
$$= \text{international joules}$$
$$1 \text{ international joule} = 1.000165 \text{ absolute joules}$$

As far as the future discussions in this text are concerned, the difference between the international units and the absolute units

are, like the difference between milliliters and cubic centimeters, so small as to have a negligible effect upon the results of calculations using them. Accordingly we shall make no attempt to distinguish between them. Nevertheless, it will be well for the student to be aware that the differences exist and to understand the reasons for their existence.

A few other special properties with their dimensions and units will be discussed as they occur in the text. The student should make himself thoroughly familiar with the definition and interrelation of the units and dimensions of the properties discussed in this chapter. In working out problems, he should invariably put in the units of each factor as it is used and should always state the units of the answer. An answer such as 0.73 may be numerically correct, but it is valueless unless it is also stated whether it represents dynes per square centimeter or calories per degree centigrade.

Problems

1. What is the weight, in dynes, of an object whose mass is 23.5 g.?
    Ans. 2.31×10^4 dynes.

2. A cube of matter 7.0 cm. on a side and having a mass of 160 g. rests on a surface. What pressure is exerted on the surface by the mass?

3. What force is necessary to give a mass of 30 g. an increase in velocity of 18 cm./sec. at the end of 3.0 sec.?

4. A mass of 20 g. is acted upon by a force of 70 dynes for 6.0 sec. What is the increase in velocity of the mass?

5. A mass of 15.0 g. falls 10.0 cm. under the action of gravity. What is its increase in energy in ergs? *Ans.* 1.47×10^5 ergs.

6. A pressure of 304 mm. of Hg equals how many (*a*) atmospheres, (*b*) g.-wt./cm.^{2}, (*c*) dynes/cm.^{2}?

7. The product of a pressure and a volume has the dimensions of energy. Express the answer to 0.200 atm. $\times$ 0.400 liter in (*a*) g.-wt. $\times$ cm., (*b*) ergs, (*c*) joules, (*d*) calories. *Ans.* (*a*) 8.26×10^4 g.-wt. $\times$ cm.

8. A pressure of 5.0 dynes/cm.^{2} on one face of a 4.0-cm. cube for 10 sec. increases its velocity by 2.0 cm./sec. What is the mass of the cube?

9. The normal temperature of the human body is 98.6°F. What is this in degrees centigrade and degrees Kelvin?

10. What temperature has the same numerical value on both the Fahrenheit and the centigrade scales? On both the Fahrenheit and absolute scales?

11. What number of grams of benzene, C_6H_6, contains the same number of molecules as does 10 g. of water, H_2O?

12. If 10.0 g. of mercury, at 100.00°C., is dropped into 10.0 g. of water, at 20.00°C., then, when equilibrium is established, the temperature of the mixture is 22.55°C. What is the specific heat of mercury?

13. Express specific heat in terms of the fundamental c.g.s. units.

14. A wire with a resistance of 90.0 ohms has a potential difference of 110 volts between its two ends. Calculate the strength of the current through the wire in (*a*) amperes, (*b*) faradays per second.

Ans. (*a*) 1.22 amp.

15. If the electrical work done while the current in Prob. 14 flows for 10 sec. could be transformed completely into heat, it would raise the temperature of how many grams of water by 5.0°C.?

CHAPTER 2

GASES

It is a familiar fact that matter is capable of existing in three different states—solid, liquid, and gaseous. Of these three states, it is in the last one—the gaseous—that matter shows the greatest regularity of behavior, and concerning this state it is most easy to make broad generalizations, or laws. The outstanding characteristic of a gas is its great sensitiveness to changes in temperature and pressure. Gases are compressible to a high degree and are infinitely expansible, filling all parts of any vessel in which they may be placed, no matter what the size of the container may be. Liquids and solids, on the other hand, show only a very limited degree of either compressibility or expansibility.

THE GAS LAWS

As a result of much careful experimentation, there has been evolved a series of statements concerning the general behavior of all gases. These statements are known as the *gas laws*. They are obeyed to a greater or less degree by all gases.

Boyle's Law. The first of these laws was stated, about 1661, by Robert Boyle. His work showed that the volume of a given mass of gas, the temperature being constant, varies inversely as the pressure on the gas. This law may be stated algebraically as follows:

$$\frac{v_1}{v_2} = \frac{p_2}{p_1} \qquad \text{or} \qquad p_1v_1 = p_2v_2 = K \text{ (a constant)} \qquad (2\text{-}1)$$

From this it is seen that an alternative statement of Boyle's law is that for a given mass of gas, at constant temperature, the product of the pressure and the volume is a constant value. This is an ideal law which is not followed exactly by any actual gas. Adherence to it becomes closer, however, at low pressures and at temperatures well above the critical temperature[1] of the

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[1] Critical temperature is defined in Chap. 3.

gas. The reasons for this behavior will be discussed in the sections on the kinetic molecular theory and the deviations from the gas laws.

Charles's Law. It was also found that if a given mass of gas is held under constant pressure its volume is directly proportional to the absolute temperature of the gas. This statement is known as Charles's law. An alternative statement of this law is that, at constant volume, the pressure of a given mass of gas varies directly as the absolute temperature. These two statements may be formulated as follows:

$$\frac{v_1}{v_2} = \frac{T_1}{T_2} \qquad \text{or} \qquad v_1 T_2 = v_2 T_1 = K' \text{ (a constant)} \qquad (2\text{-}2)$$

or

$$\frac{p_1}{p_2} = \frac{T_1}{T_2} \qquad \text{or} \qquad p_1 T_2 = p_2 T_1 = K'' \text{ (a constant)} \qquad (2\text{-}3)$$

The relationship between temperature and pressure affords one means of deriving the absolute, or Kelvin, scale of temperature. If the volume of a given mass of gas is held constant it is found that for each degree centigrade fall in temperature the pressure of the gas decreases by very nearly $\frac{1}{273}$ of its pressure at 0°C. If gases followed this rule at all temperatures it is apparent that at approximately −273°C. the pressure of the gas would be zero. Actually, all known gases liquefy before reaching this point and, furthermore, the temperature has never been attained, although some workers have come within a few thousandths of a degree of it. Nevertheless, this temperature has a theoretical significance in that it represents the point at which all molecular motion ceases and there can be no lower temperature. This temperature, therefore, is known as the *absolute zero* and is the starting point of the absolute, or Kelvin, scale.

Standard Conditions. Since the volume of a gas is so markedly affected by changes in temperature and pressure, it is necessary, in comparing different volumes of gases, that they should be at the same temperature and pressure. The *standard conditions*, to which all gas volumes are commonly reduced for purposes of comparison, are as follows:

Standard pressure = 1.000 atm., or 760.0 mm. of Hg
Standard temperature = 0°C., or 273°K.

If a gas volume is given at a temperature and pressure other than 0°C. and 760 mm. of Hg, it is possible, by the application of Boyle's and Charles's laws, to calculate what the gas volume would be at standard conditions.

Example. A gas occupied 100 cm.³ at 20°C. and 740 mm. of Hg pressure. What is its volume at standard conditions? (1) Hold the temperature constant at 20°C., and apply Boyle's law.

$$\frac{100 \text{ cm.}^3}{x} = \frac{760 \text{ mm. Hg}}{740 \text{ mm. Hg}} \qquad x = 97.4 \text{ cm.}^3$$

That is, the gas occupies 97.4 cm.³ at 20°C. and 760 mm. of Hg pressure. (2) Hold the pressure constant at 760 mm. of Hg, and apply Charles's law.

$$\frac{97.4 \text{ cm.}^3}{y} = \frac{293°\text{K.}}{273°\text{K.}} \qquad y = 90.7 \text{ cm.}^3$$

That is, this same mass of gas occupies 90.7 cm.³ at standard conditions.

The Ideal-gas Equation for a Specific Gas. For a given mass of some particular gas, the formulation of Boyle's and Charles's laws may be combined as follows. Let the initial state of the gas be represented by p_1, v_1, and T_1, and let it change to a second state, represented by p_2, v_2, T_2, in the following steps. First, holding the temperature constant at T_1, let the pressure change from p_1 to p_2. This will cause the volume to change to a new value x, and according to Boyle's law

$$p_1 v_1 = p_2 x \qquad \text{or} \qquad x = \frac{p_1 v_1}{p_2}$$

Then, holding the pressure constant at p_2, let the temperature change from T_1 to T_2. This will cause a second volume change from x to v_2, and according to Charles's law

$$\frac{x}{T_1} = \frac{v_2}{T_2}$$

Substituting in this second expression, the value for x obtained from the first gives

$$\frac{p_1 v_1}{p_2 T_1} = \frac{v_2}{T_2}$$

or

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2} = K \text{ (a constant)}$$

This latter expression simply states that, for a given mass of

gas, the product of pressure and volume divided by temperature is a constant value. This is the *ideal-gas equation* for a specific gas. It is more commonly written as

$$pv = KT \qquad (2\text{-}4)$$

where T is in degrees absolute and K is a constant whose value depends on the mass and chemical composition of the gas. This equation would be followed exactly by an ideal gas but is obeyed only approximately by an actual gas. The closeness of this approximation increases as the pressure falls and the temperature rises.

The General Ideal-gas Equation. The specific-gas equation contains a constant K, which has different values for different gases. It would be extremely useful if an expression could be devised that contained a constant which had the same value for all gases. This could be accomplished if some standard for quantity of gas could be taken such that that quantity of any gas would occupy, at the same temperature and pressure, the same volume as would a like quantity of any other gas. In other words, the value of the expression pv/T would be the same for this standard quantity of all gases.

The solution to this problem was offered by the Italian physicist Avogadro when he stated that, under the same pressure and temperature, equal volumes of all gases contain the same number of molecules. This statement, in common with the other gas laws, is true only for gases that behave as ideal gases. However, as we shall see later, it is possible, by proper selection of conditions, to make the behavior of actual gases approach ideality.

It has already been shown that 1 mole of any substance contains the same number of individual molecules as does 1 mole of any other substance. From Avogadro's statement, it follows that, under the same conditions of temperature and pressure, 1 mole of any gas must occupy the same volume as 1 mole of any other gas. This means that if the mole is taken as the unit of quantity for a gas, then, for 1 mole of any gas, $pV/T = R$, or $pV = RT$, where R is known as the *molal gas constant* and is the same for all gases. In these expressions V represents the volume of 1 mole of the gas. If the number of moles of gas used is some number, n, not equal to 1, the equation becomes

$$pv = nRT \qquad (2\text{-}5)$$

in which v refers to the volume of the number of moles of gas being considered.

Equation (2-5) is the *general ideal-gas equation* which would be followed by ideal gases and is followed fairly closely by actual gases at low pressures and at temperatures well above their critical temperature.

The Gram-molecular Volume.   The volume occupied by 1 mole of any ideal gas, at standard conditions of temperature and pressure, is known as the *gram-molecular volume.*   Oxygen has been chosen as the standard for molecular weights and has arbitrarily been assigned the value 32.0000 as its molecular weight.   It has been determined that 1 mole, or 32.0000 g., of oxygen, if it behaved as an ideal gas, would occupy 22.414 liters at standard conditions.   Therefore, 1 mole of any other gas, if it behaved as an ideal gas, would occupy the same volume at standard conditions.   This volume, 22.414 liters, is known as the gram-molecular volume.   To determine the molecular weight of any gas it is necessary simply to find what mass of that gas, if it behaved as an ideal gas, would occupy 22.414 liters at standard conditions. A method by which this may be accomplished will be described at the end of this chapter.

The Significance of R.   If Eq. (2-5) is solved for R, it gives $R = pv/nT$.   The product pv represents energy or work.   Therefore, R must represent *work per mole per degree.*   To visualize what this work is, consider 1 mole of an ideal gas at p and T. Under these conditions

$$pV = RT$$

Now, keeping the pressure constant, let the temperature rise 1°C. to $(T + 1)$.   The volume will increase to V_1, and the gas will do work in expanding against the pressure p.   The amount of this work is equal to $p(V_1 - V)$.   Under the new conditions

$$pV_1 = R(T + 1)$$

Subtracting the first equation from the second gives

$$pV_1 - pV = R(T + 1) - RT$$

or

$$p(V_1 - V) = RT + R - RT = R$$

From this it appears that R equals the work done by 1 mole of an

ideal gas in expanding against a constant pressure as the result of a rise of 1°C. in the temperature. This value is independent of the pressure and the nature of the gas.

It is now apparent what work the product pv stands for in the expression $pv = nRT$. It represents the amount of work done by n moles of an ideal gas in expanding against constant pressure as the temperature rises from 0°K. to the temperature at which the gas is observed.

Values of R. Since R represents work per mole per degree, it must be expressible in terms of one of the work units. The value of R may be calculated as follows. It has already been shown that 1 mole of an ideal gas, at standard conditions, occupies 22.414 liters. Substituting these values in the gas equation and solving for R gives

$$R = \frac{pv}{nT} = \frac{1.00 \text{ atm.} \times 22.414 \text{ liters}}{1.00 \text{ mole} \times 273°\text{K.}} = 0.0821 \frac{\text{liter} \times \text{atm.}}{\text{mole} \times °\text{K.}}$$

Other commonly used values are

$$R = 8.478 \times 10^4 \frac{\text{g.-wt.} \times \text{cm.}}{\text{mole} \times °\text{K.}}$$

$$R = 8.314 \times 10^7 \frac{\text{ergs}}{\text{mole} \times °\text{K.}}$$

$$R = 8.314 \frac{\text{joules}}{\text{mole} \times °\text{K.}}$$

$$R = 8.314 \frac{\text{volt} \times \text{coulombs}}{\text{mole} \times °\text{K.}}$$

$$R = 1.987 \frac{\text{cal.}}{\text{mole} \times °\text{K.}}$$

The Use of the Gas Equation. The gas equation is one of the most valuable and widely used expressions in physical chemistry. Reference to it, in either its original form or some modification, will appear constantly in the succeeding work in this text. The student should familiarize himself with its potentialities and, by the doing of problems, gain as much practice as possible in its use.

Example 1. What is the volume of 1.00 mole of gas at 23°C. and 770 mm. of Hg pressure? (Note that p, v, and R must be expressed in consistent units.)

$$v = \frac{nRT}{p} = \frac{1.00 \text{ mole} \times 0.0821 \frac{\text{liter} \times \text{atm.}}{\text{mole} \times °\text{K.}} \times 296°\text{K.}}{{}^{770}\!/_{760} \text{ atm.}} = 23.9 \text{ liters}$$

Example 2. At what temperature will 0.500 mole of gas occupy 10.0 liters at 700 mm. of Hg pressure?

$$T = \frac{pv}{nR} = \frac{700/760 \text{ atm.} \times 10.0 \text{ liters}}{0.500 \text{ mole} \times 0.0821 \frac{\text{liter} \times \text{atm.}}{\text{mole} \times {}^{\circ}\text{K.}}} = 224{}^{\circ}\text{K.} = -49{}^{\circ}\text{C.}$$

Graham's Law. The statement of Graham's law is the result of the observation of the speeds of diffusion of various gases through small openings. It was found that under the same conditions of temperature and pressure the speeds of diffusion of two different gases are inversely proportional to the square roots of their densities.

$$\frac{c_1}{c_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} \tag{2-6}$$

An alternative statement of the law is that the times of diffusion of equal volumes of two gases, at the same temperature and pressure, are directly proportional to the square roots of their densities.

$$\frac{t_1}{t_2} = \frac{\sqrt{d_1}}{\sqrt{d_2}} \tag{2-7}$$

Since the density of a gas is directly proportional to its molecular weight, the molecular weights M_1 and M_2 may be substituted for d_1 and d_2.

Example. What are the relative speeds of diffusion of hydrogen and oxygen under the same conditions?

$$\frac{c_{H_2}}{c_{O_2}} = \frac{\sqrt{M_{O_2}}}{\sqrt{M_{H_2}}} = \frac{\sqrt{32}}{\sqrt{2.0}} = \frac{4}{1}$$

Dalton's Law of Partial Pressures. Dalton's law states that when two or more gases which do not react chemically with each other are mixed, each gas behaves independently of the others, and shows the same pressure that it would show if it were present alone in the volume occupied by the whole mixture of gases. This pressure is known as the *partial pressure* of the gas in the mixture. (Sometimes the word *tension* is used as synonymous with partial pressure.) The total pressure is equal to the sum of the partial pressures of the component gases.

$$P = p_a + p_b + p_c \tag{2-8}$$

Dalton's law is also an ideal law which is followed approximately by actual gases under ordinary conditions.

The partial pressure of any gas in a mixture may be calculated as follows. Let the mixture contain n_a moles of A, n_b moles of B, and n_c moles of C. Let P represent the total pressure on the mixture. Then p_a, the partial pressure of A, is given by the expression $p_a = P[n_a/(n_a + n_b + n_c)]$. The expression $n_a/(n_a + n_b + n_c)$ is known as the *mole fraction* of A in the mixture and is more commonly written as n_a/N, where N represents the total number of moles present, *i.e.*,

$$N = n_a + n_b + n_c$$

The partial pressure of B is given by the expression $p_b = P(n_b/N)$, that of C by $p_c = P(n_c/N)$.*

Example 1. Calculate the partial pressure of each gas in a mixture containing 2.50 moles of nitrogen, 1.00 mole of oxygen, and 0.500 mole of carbon dioxide. The total pressure is 2.00 atm.

$$p_{N_2} = P\frac{n_{N_2}}{N} = 2.00 \times \frac{2.50}{4.00} = 1.25 \text{ atm.}$$

$$p_{O_2} = P\frac{n_{O_2}}{N} = 2.00 \times \frac{1.00}{4.00} = 0.50 \text{ atm.}$$

$$p_{CO_2} = P\frac{n_{CO_2}}{N} = 2.00 \times \frac{0.500}{4.00} = 0.25 \text{ atm.}$$

If the oxygen and carbon dioxide were removed, the nitrogen would fill the whole container, but the pressure would then be only 1.25 atm.

Example 2. If the temperature in Example 1 is 0°C., calculate the volume of the container. This may be done by using either the total number of moles and the total pressure, or the number of moles of any one gas and its partial pressure.

$$v = \frac{NRT}{P} = \frac{4.00 \text{ moles} \times 0.0821 \frac{\text{liter} \times \text{atm.}}{\text{mole} \times °\text{K.}} \times 273°\text{K.}}{2.00 \text{ atm.}} = 44.8 \text{ liters}$$

$$v = \frac{n_{O_2}RT}{p_{O_2}} = \frac{1.00 \text{ mole} \times 0.0821 \frac{\text{liter} \times \text{atm.}}{\text{mole} \times °\text{K.}} \times 273°\text{K.}}{0.500 \text{ atm.}} = 44.8 \text{ liters}$$

Example 3. A gas measured over water occupies a volume of 300 cm.³ at 18°C. and 740.0 mm. of Hg pressure. Calculate the number of moles of gas present. The vapor pressure of water, at 18°C., is 15.3 mm. of Hg.

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* The mole fraction of a gas in a mixture is directly proportional to its per cent by volume in that mixture. Therefore, in the above expressions, we may substitute for mole fraction the expression $x/100$, where x is the per cent by volume of the gas in the mixture.

The partial pressure of the gas is equal to the total pressure minus the vapor pressure of water.

$$p_1 = 740.0 - 15.3 = 724.7 \text{ mm. of Hg}$$

Therefore the number of moles of gas is

$$n_1 = \frac{p_1 v}{RT} = \frac{724.7/760 \text{ atm.} \times 0.300 \text{ liter}}{0.0821 \dfrac{\text{liter} \times \text{atm.}}{\text{mole} \times {}^\circ\text{K.}} \times 291^\circ\text{K.}} = 0.012 \text{ mole}$$

THE KINETIC MOLECULAR THEORY OF GASES

In attempting to arrive at a physical picture of the nature of gases, which would explain adequately their observed behavior as stated in the gas laws, there has been put forth the *kinetic molecular theory of gases*. The main points of this theory are

1. Gases are composed of discrete particles called molecules. All the molecules of any one gas are identical in nature.

2. The molecules in a gas are relatively far apart, and their aggregate volume is negligible compared with the volume of the containing vessel. (This is true only at low densities of the gas.)

3. The molecules are in constant random motion, in straight lines. The speed of this motion is directly proportional to the square root of the absolute temperature of the gas.

4. The molecules are perfectly elastic, rebounding with undiminished speed when they hit each other or the walls of the containing vessel.

5. The molecules exert no attractive force on each other. (This is not strictly true.)

6. The pressure of the gas is the result of the impacts of the molecules on the walls of the containing vessel.

A Gas Equation Derived from the Kinetic Molecular Theory. As a means of demonstrating the validity of the assumptions stated in the kinetic molecular theory, they may be used to derive a theoretical gas equation. If such a theoretical equation agrees with the one derived from the experimentally determined gas laws, it encourages belief that the picture of a gas, as described in the kinetic molecular theory, is a correct one. The theoretical equation may be derived as follows.

Select a cubical vessel of side l (Fig. 2-1) and imagine it to contain n molecules of an ideal gas, each molecule having the mass m. At some constant temperature the velocities of the individual molecules may vary widely, but their average velocity c will be characteristic of the gas at that temperature. Select one of these

molecules, and picture it as moving in the direction and with the velocity indicated by the arrow c. This motion may be resolved into three components, indicated by the arrows x, y, z, perpendicular to the faces of the cube, so that $c^2 = x^2 + y^2 + z^2$. Consider now the x component of this motion; in other words, picture the molecule as moving perpendicularly to the left face of the cube with a velocity x. If it hits this wall and rebounds with undiminished speed in the opposite direction, the total change in the velocity of the molecule is $2x$. The number of times per second that this velocity change occurs is equal to the speed of the molecule divided by the distance between opposite faces of the cube. This is equal to x/l. Therefore the change in velocity per second (or acceleration) of the molecule is

$$2x \times x/l = 2x^2/l$$

The force exerted on these opposite faces of the cube by the molecule is

Fig. 2-1. The motion of a gas molecule.

equal to the mass of the molecule multiplied by its acceleration, or $2mx^2/l$.

Calculating, in the same way, the force resulting from the motion of the molecule along the y and z components gives as the total force on all six faces of the cube, caused by the motion of this single molecule,

$$\frac{2mx^2}{l} + \frac{2my^2}{l} + \frac{2mz^2}{l} = \frac{2mc^2}{l}$$

The force produced by all n molecules will be $2mnc^2/l$. The pressure, or force per unit area, is the total force divided by the area of the six faces of the cube. This area is $6l^2$. Therefore the pressure p exerted by the gas is

$$p = \frac{2mnc^2}{l \times 6l^2} = \frac{1}{3}\frac{mnc^2}{l^3}$$

Since the cube of a length represents a volume, we may rewrite this as
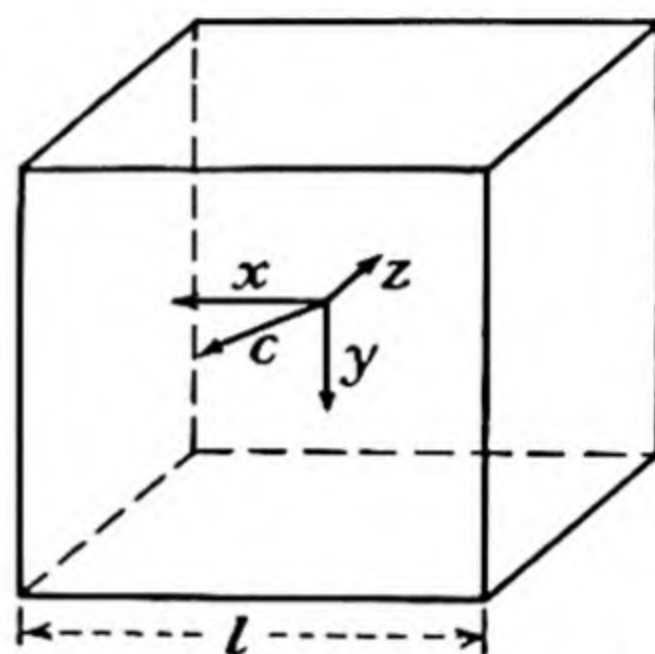
$$p = \frac{1}{3}\frac{mnc^2}{v}$$

or

$$pv = \tfrac{1}{3}\, mnc^2 \tag{2-9}$$

Equation (2-9) is a theoretical expression which is at least similar in form to the experimentally derived $pv = nRT$. To test the validity of this new equation, and also of the theory on which it is based, we can see if it agrees with the gas laws.

Boyle's Law. For a given mass of gas, at constant temperature, all the factors on the right-hand side of Eq. (2-9) are constant. Therefore $pv = K$ (a constant). This is Boyle's law.

Charles's Law. For a given mass of gas the only variable on the right-hand side of Eq. (2-9) is c, the velocity of the molecules. This is directly proportional to the square root of the absolute temperature. Therefore, if p is held constant, v must vary directly as the absolute temperature. This is Charles's law.

Graham's Law. Solving Eq. (2-9) for c gives

$$c = \sqrt{\frac{3pv}{mn}}$$

The product mn equals the total mass of the gas. It has already been shown that density equals mass divided by volume. Therefore, $v/mn = 1/d$ and the above expression becomes

$$c = \sqrt{\frac{3p}{d}} \tag{2-10}$$

Stated in words, Eq. (2-10) is Graham's law, *viz.*, the speed of the molecules of a gas is inversely proportional to the square root of its density.

Molecular Velocities. Equation (2-10) may be used to calculate the average speed of the molecules of a gas, as the following example will show. This example also illustrates the importance of using correct units and of stating the units of each factor in the expression. In order to get a significant answer in centimeters per second, it is necessary that pressure be expressed in dynes per square centimeter and density in grams per cubic centimeter.

Example. Calculate the speed of the hydrogen molecule at standard conditions.

$$p = 1 \text{ atm.} = 1.013 \times 10^6 \frac{\text{dynes}}{\text{cm.}^2} = 1.013 \times 10^6 \frac{\text{g.}}{\text{cm.} \times \text{sec.}^2}$$

At standard conditions, 1 mole (2.016 g.) of hydrogen occupies 22.414 liters (22,414 cm.^{3}). Therefore, $d = \dfrac{2.016}{22,414}$ g./cm.^{3}

$$c = \sqrt{\frac{3 \times 1.013 \times 10^6 \dfrac{\text{g.}}{\text{cm.} \times \text{sec.}^2}}{\dfrac{2.016}{22,414} \dfrac{\text{g.}}{\text{cm.}^3}}} = \sqrt{3.38 \times 10^{10} \frac{\text{cm.}^2}{\text{sec.}^2}}$$

$$= 1.84 \times 10^5 \text{ cm./sec.}$$

DEVIATIONS FROM THE GAS LAWS

It has already been stated that actual gases follow the gas laws only approximately. The deviations in the behavior of actual gases from that stated in Boyle's law are typical.

For 1 mole of an ideal gas Boyle's law requires that the product pV remain constant at all pressures if the temperature remains constant. In terms of the ideal-gas equation this can be stated as $pV/RT = 1$. The behavior of actual gases may vary widely from that of the ideal gas. This is illustrated in Fig. 2-2, in
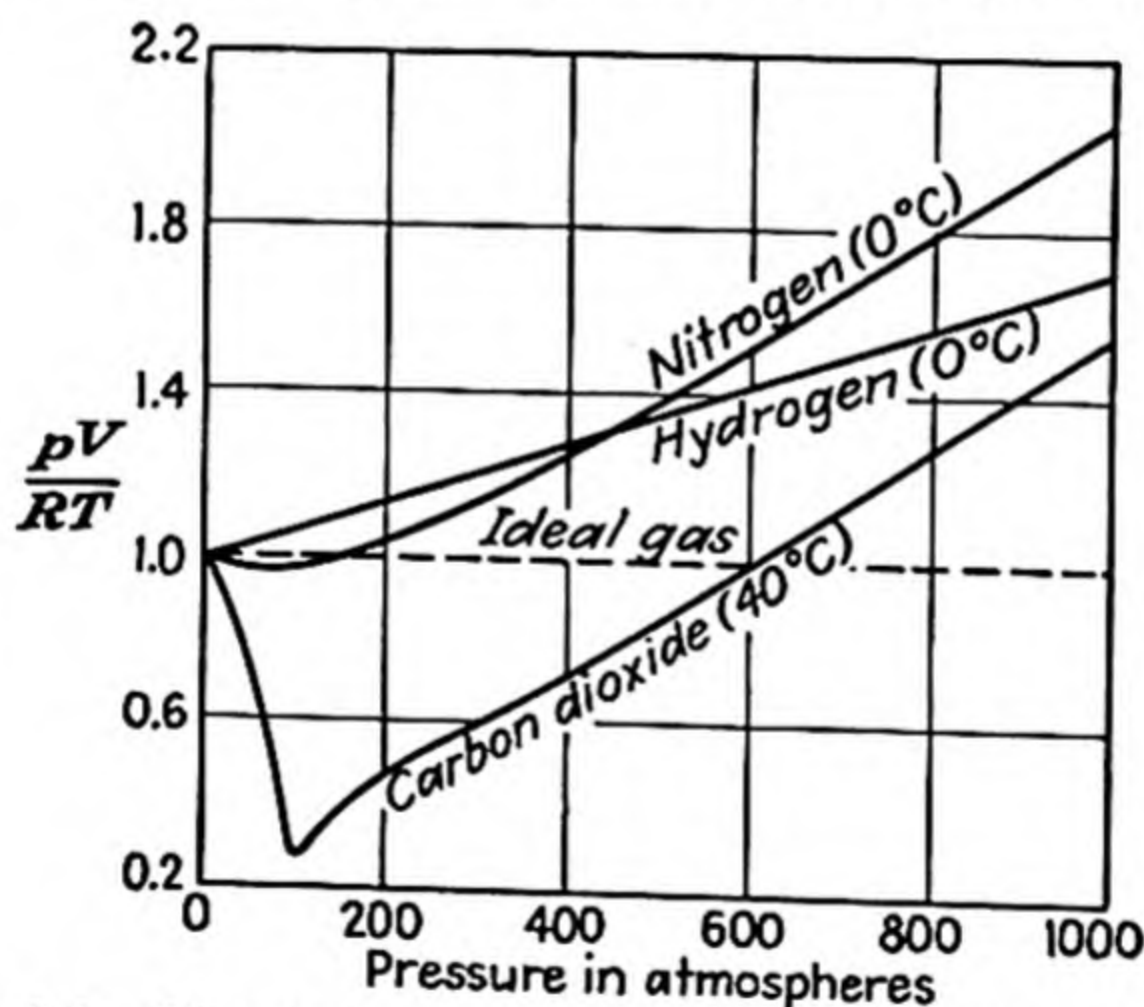

FIG. 2-2. The deviation of actual gases from Boyle's law.

which the values of pV/RT for 1 mole of each of three gases, at the temperatures indicated, are plotted against the pressure. The data for carbon dioxide are selected at 40°C. because at temperatures below 31°C. the gas liquefies before a pressure of 73 atm. is reached.

For an ideal gas the value of pV/RT should equal unity at all pressures, as indicated by the dotted line. It will be noted that

in the case of carbon dioxide and nitrogen the curves drop to a minimum, below the ideal value, and then rise continually, going above the ideal value as the pressure increases. The curve for hydrogen shows no minimum but is always above the ideal value. However, at a sufficiently low temperature the curve for hydrogen also shows a minimum. Conversely, if the temperature is sufficiently high the curves for nitrogen and carbon dioxide will show no minimum and will always lie above the ideal value. Values
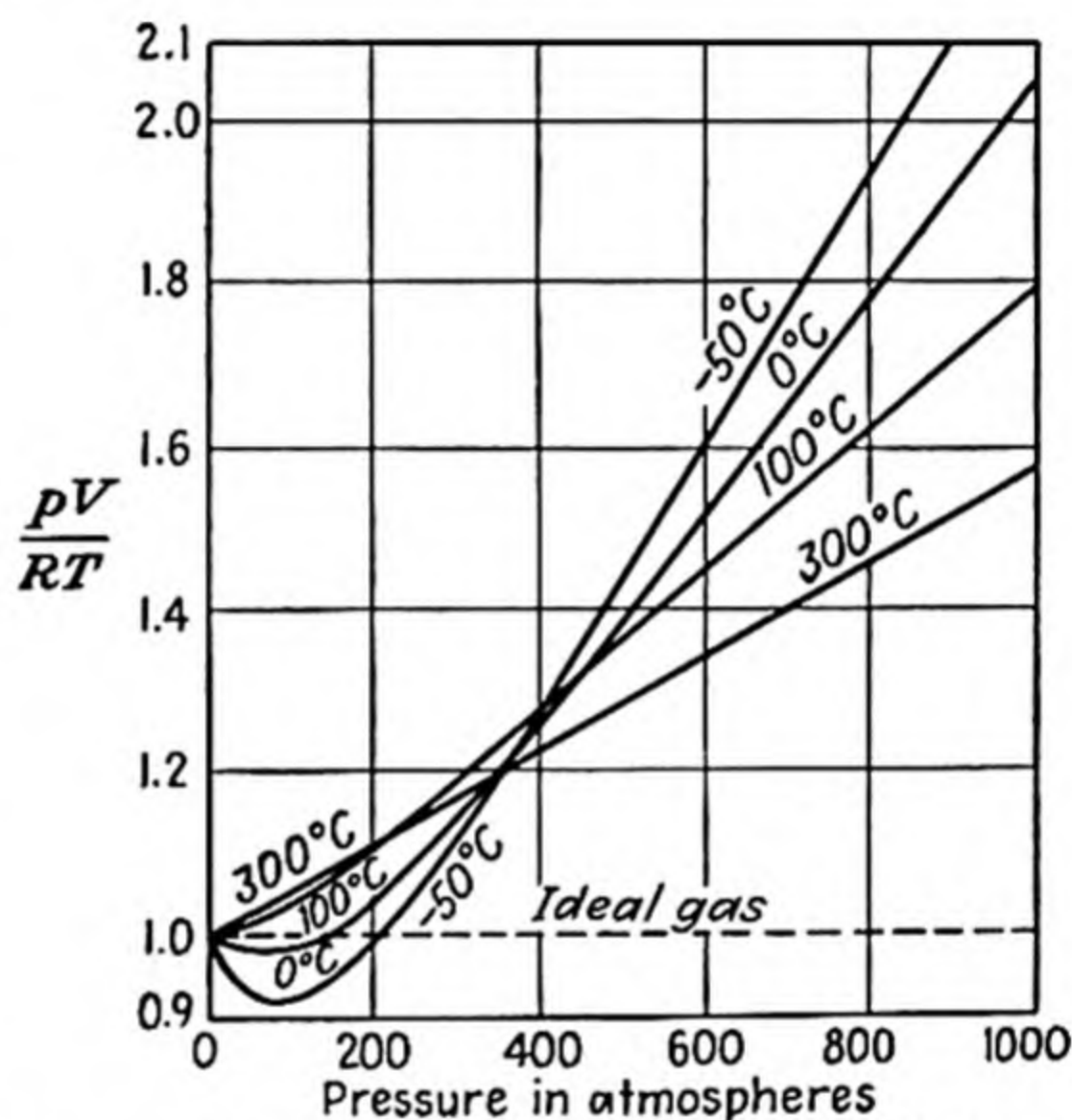

FIG. 2-3. Influence of temperature on the deviations of nitrogen from Boyle's law.

for pV/RT of less than unity indicate that the actual gas is more compressible than the ideal; values greater than unity indicate that the actual gas is less compressible than the ideal.

The influence of temperature upon the deviations of nitrogen from Boyle's law is shown in Fig. 2-3, in which the values of pV/RT for 1 mole of the gas at various temperatures are plotted against the pressure. It will be noted that the curves for −50 and 0°C. show a minimum, but that those for 100 and 300°C. show no minimum. Similar variations with temperature have been observed for other gases, and it is probable that the behavior is general.

The curve, at 51°C., for nitrogen approximates very closely the curve for an ideal gas for pressures less than 50 atm. In other

words, at this temperature and in this pressure range, the gas obeys Boyle's law. The particular temperature at which this is true is called the *Boyle point* for the gas. At temperatures below the Boyle point the pV/RT curve shows a minimum; at temperatures above the Boyle point the curve shows no minimum and is always above the curve for the ideal gas. Different gases have different values for their Boyle points; that for hydrogen is $-165.9°C$.

The explanation for these deviations shown by actual gases is found in the assumptions made in the statements of the kinetic molecular theory. One of these assumptions is that no attractive forces exist between the molecules. Such attractive forces, known as *van der Waals forces*, do exist. When the molecules are fairly close together, and at temperatures that are not so high that their thermal motion counteracts the van der Waals forces, these forces retard the motion of the molecules hitting the walls of the containing vessel, making the observed pressure of the gas less than that expected from Boyle's law. Under these conditions $pV < RT$.

A second assumption is that the aggregate volume of the molecules of a gas is negligible compared with the volume of the containing vessel. While this is approximately true when the molecules are widely separated, if the gas is highly compressed the space between the molecules is decreased and their volume becomes more and more significant. Under these conditions the effect of the volume of the molecules is to decrease appreciably the free space available for their motion. Accordingly, the observed volume V is appreciably greater than the ideal volume which must be used if Boyle's law is to hold. At densities that are sufficiently high so that the excess of observed volume over ideal volume more than offsets the decrease, due to van der Waals forces, of observed pressure under ideal pressure, $pV > RT$.

At very low pressures the gas molecules are widely separated and both their attraction for each other and their volume become negligible. Accordingly, as the pressure is decreased, the behavior of the gas approximates more and more closely that of the ideal gas. Theoretically, at zero pressure all gases behave as ideal gases. This is indicated in Figs. 2-2 and 2-3, where it is seen that all the curves approach the ideal value at zero pressure.

Methods of Compensating for Deviations from the Gas Laws.
In working with actual gases there are two common ways of compensating for these deviations. One is to alter the ideal-gas equation so that it will fit the conduct of the gas; the other is to alter the conditions of the gas so that its conduct will fit the ideal-gas equation. For all ordinary gas problems the uncorrected gas equation is probably sufficiently accurate, but for more exact work one of the following methods may be used.

1. *van der Waals's Equation.* The Dutch chemist van der Waals applied corrections to the ideal-gas equation for 1 mole of gas to make it represent more closely the conduct of actual gases. To compensate for the tendency of the forces of intermolecular attraction to make the observed pressure less than the ideal pressure he introduced the term a/V^2 to be added to the observed pressure. In this term, a is a constant characteristic of the gas in question. Its dimensions are such that when it is divided by the square of a volume the result is a pressure. The units in which a is expressed must be consistent with those used in the rest of the equation, *i.e.*, if pressure is in atmospheres and volume in liters then a must be in liters^2 × atmospheres.

To compensate for the tendency of the volume of the molecules to make the observed volume of a gas more than the ideal volume, van der Waals introduced the term b, to be subtracted from the observed volume. The value of b is estimated to be approximately four times the actual volume of the molecules of 1 mole of gas. It has the dimensions of a volume, and the units in which it is expressed must be consistent with those used in the rest of the equation.

The values of a and b are approximately constant for any one gas but vary for different gases and must be determined experimentally for each gas.

With the introduction of these corrections the ideal-gas equation for 1 mole of gas becomes

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \tag{2-11}$$

known as van der Waals's equation. It will be noted that at low pressures, *i.e.*, at large values of V, the value of a/V^2 becomes negligible compared with p, and b becomes negligible compared with V, so that van der Waals's equation approaches $pV = RT$.

At ordinary temperatures and pressures van der Waals's equation represents the observed conduct of actual gases more closely than does the ideal-gas equation.

Other modifications of the ideal-gas equation have been proposed which give better results than does van der Waals's equation in certain situations. For these equations the student is referred to more comprehensive books on physical chemistry.[1]

2. *The Method of Limiting Densities.* This method is used particularly for the accurate determination of molecular weights of gases and is based on the idea that all gases at zero pressure follow the ideal-gas equation. If this equation is to be used for the determination of molecular weights, it may be rewritten as follows, since n, the number of moles of gas, is equal to the mass of the gas divided by its molecular weight:

$$pv = \frac{\text{mass}}{\text{mol. wt.}} \times RT$$

or

$$\text{Mol. wt.} = \frac{\text{mass}}{v} \times \frac{RT}{p}$$

But mass divided by volume equals density, so

$$\text{Mol. wt.} = \frac{d}{p} RT \tag{2-12}$$

For an ideal gas, at constant temperature, the value of the ratio d/p is a constant at all pressures. For an actual gas, at low pressures, the value of d/p is approximately a linear function of the pressure. The values of the ratio for both the ideal gas and the actual gas would be the same at zero pressure. If the density of the gas, at some constant temperature, is determined at several different low pressures, and the values of the ratio d/p are plotted against p, a straight line is obtained as indicated by AB in Fig. (2-4). The behavior of an ideal gas is indicated by the line CD, along which the value of d/p is a constant at all pressures. The line for the actual gas may be extrapolated to zero pressure along AD. The value of the ratio d/p at zero pressure is that which the gas, if it behaved as an ideal gas, should show at any finite pressure. This value may then be substituted in Eq. (2-12) to

[1] For example, S. Glasstone, "Textbook of Physical Chemistry," 2d ed., pp. 288–298, D. Van Nostrand Company, Inc., New York, 1946.

give accurate values of the molecular weight. The temperature to be used in Eq. (2-12) is that at which the density determinations were made.
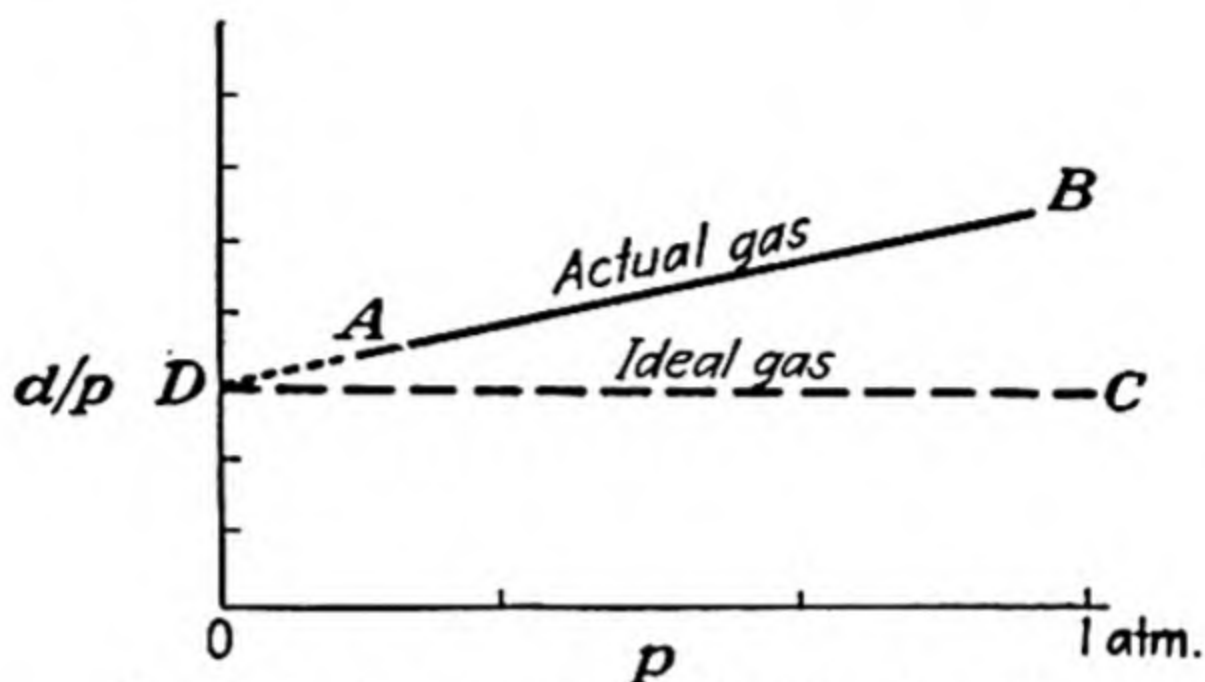

Fig. 2-4. The method of limiting densities.

Problems

1. A gas occupies 0.300 liter at 20°C. and 720 mm. of Hg pressure. What volume will it occupy at standard conditions? *Ans.* 265 ml.

2. A gas occupies 0.700 liter at standard conditions. What volume will it occupy at −10°C. and 800 mm. of Hg pressure?

3. What mass of nitrogen is contained in 10.50 liters at 18°C. and a pressure of 0.487 atm.?

4. At what pressure will 10.0 liters contain 10.0 g. of carbon dioxide at 25°C.?

5. A liter of methane, CH_4, diffuses through a pinhole in 42.0 min. How long will it take a liter of carbon dioxide, at the same temperature and pressure, to diffuse through the same pinhole?

6. A flask contains a mixture of nitrogen and oxygen. The total pressure is 2.000 atm. If the oxygen is removed, the pressure drops to 1.500 atm. and the mass of the flask and contents decreases by 10.0 g. The temperature was 10°C. What was the volume of the flask and the original mass of its contents?

7. It can be shown that the kinetic energy ($\frac{1}{2}mc^2$) of all molecules is the same at the same temperature. Using this fact, show that the expression $pv = \frac{1}{3}mnc^2$ is in agreement with Avogadro's statement.

8. Since temperature affects the speed of molecules, why does not temperature appear in Eq. (2-10)?

9. Calculate the speed, in centimeters per second, of the nitrogen molecule at standard conditions. What change in this speed would be caused by an increase in pressure to 2 atm. if the temperature does not change?

10. Calculate from the ideal-gas equation and also from van der Waals's equation the pressure, in atmospheres, at which 1.00 mole of carbon dioxide occupies a volume of 1.320 liters at 31°C. Which of these two values is nearest to the observed pressure of 17.22 atm.? For carbon dioxide the value of $a = 3.61$ liters² × atm., the value of $b = 4.28 \times 10^{-2}$ liter.

11. From the following data, calculate the exact molecular weight of methyl fluoride by the method of limiting densities.

Pressure, atm.	Mass of 1.0000 liter of CH_3F at 0°C., g.
1.0000	1.5451
0.6667	1.0238
0.3333	0.5089

(In Eq. (2-12) the values of p, d, and R must be expressed in consistent units.)

CHAPTER 3

LIQUIDS

When a gas is cooled, the speed of the molecules and, therefore, their kinetic energy decrease. If, at the same time, pressure is applied to the gas, its molecules are brought closer together and the force of attraction between them is thereby increased. If these two processes of cooling and compression are continued, a point will be reached where the kinetic energy is no longer able to overcome the force of intermolecular attraction. At this point, the molecules are no longer able to move freely about but are held close together and are limited in their motion. The substance then is said to have passed from the gaseous to the liquid state. This state resembles the gaseous condition in that a substance in the liquid state has no definite shape and will flow freely, but differs in that liquids have a definite volume which varies but slightly with changes of temperature and pressure. The behavior of liquids is not subject to generalizations such as were made in the case of gases. Each liquid behaves in its own peculiar way, so that it has not been possible to formulate liquid laws comparable to the gas laws. There are, however, certain properties that all liquids show, and a knowledge of these properties is important.

Critical Temperature and Critical Pressure. It has been shown that the kinetic energy of the molecules of a gas decreases as the temperature drops. For each gas there is a temperature above which the kinetic energy of the molecules is so large that no matter how close the molecules are brought together by pressure their attractive force is not sufficient to cause the gas to liquefy. This temperature is known as the *critical temperature* of the substance. No pressure is great enough to cause a gas to liquefy above its critical temperature. At its critical temperature a gas may be liquefied if enough pressure is put on it. The amount of pressure just necessary to liquefy a gas at its critical temperature is known as the *critical pressure* of the substance. The term *vapor* is sometimes used to describe a gas below its critical temperature.

As the temperature is decreased below the critical temperature, less and less pressure is required to bring about liquefaction. Eventually a temperature is reached at which a pressure of 1 atm. will cause the gas to liquefy. This temperature is known as the *normal boiling point* of the substance.[1] Table 3-1 gives the critical temperatures, critical pressures, and boiling points of some common substances.

TABLE 3-1. CRITICAL TEMPERATURES, CRITICAL PRESSURES, AND BOILING POINTS OF SOME GASES

Substance	Critical temperature, °C.	Critical pressure, atm.	Boiling point, °C.
Hydrogen............	−239.9	12.8	−252.7
Nitrogen............	−147.1	33.5	−195.8
Oxygen..............	−118.8	49.7	−183.0
Carbon dioxide.......	+31.1	73.0	−78.5 (solid sublimes)
Ammonia............	+132.4	111.5	−33.3
Sulfur dioxide.........	+157.2	77.7	−10.0
Water...............	+374.0	217.7	+100.0

Evaporation. If any liquid is left in an open container, it will eventually pass completely into the gaseous state, or will *evaporate*. There is a wide difference in the speeds with which various liquids do this, the evaporation of ether being very rapid, whereas that of mercury is extremely slow. The steps by which this process of evaporation takes place are worth considering. The average velocity of the molecules of a liquid is determined by the absolute temperature of the liquid, but the individual molecules vary considerably in their speeds. Some of the faster molecules, as they reach the surface of the liquid, possess sufficient kinetic energy to overcome the attraction of the surrounding molecules and leave the surface as a vapor. The remaining molecules of the liquid now have a lower average velocity, and therefore the temperature of the liquid will be decreased. The liquid will absorb heat from its surroundings and continue to send out molecules as a vapor until the liquid has entirely

[1] A second definition of boiling point will be given in the section on boiling points. Both definitions, however, refer to the same temperature for a given substance.

disappeared. This absorption of heat is especially striking in the case of volatile liquids such as ether. Less noticeable, but more important, is the cooling of the body surface on warm days by the evaporation of perspiration.

Heat of Vaporization. The amount of heat that is absorbed when 1 g. of a liquid vaporizes is known as the *heat of vaporization* of that liquid. This heat is measured in calories. The quantity required varies with the liquid and also with the temperature at which evaporation takes place. The heat of vaporization of water at 100°C. is 540 cal./g. This same quantity of heat is released when 1 g. of steam condenses to water at 100°C.

Vapor Pressure. If a closed container is partially filled with a liquid, evaporation will take place as before, but now the molecules of the vapor are confined so that as they move about some will hit the surface of the liquid and be trapped by it, thus passing from the vapor to the liquid state. If enough liquid is present, a point will eventually be reached where the number of molecules returning to the surface per second just equals the number leaving it. This is a state of equilibrium, and no apparent further change takes place. The molecules of the vapor exert a pressure on the surface of the liquid and on the walls of the container just as would any gas. This pressure, exerted at equilibrium by the molecules of the vapor of a liquid, is known as the *vapor pressure* of that liquid. If other gases are also present in the space above the liquid, the pressure of the vapor molecules is known as the *partial pressure* of the vapor of the liquid. The whole mixture of gases and vapor follows Dalton's law.
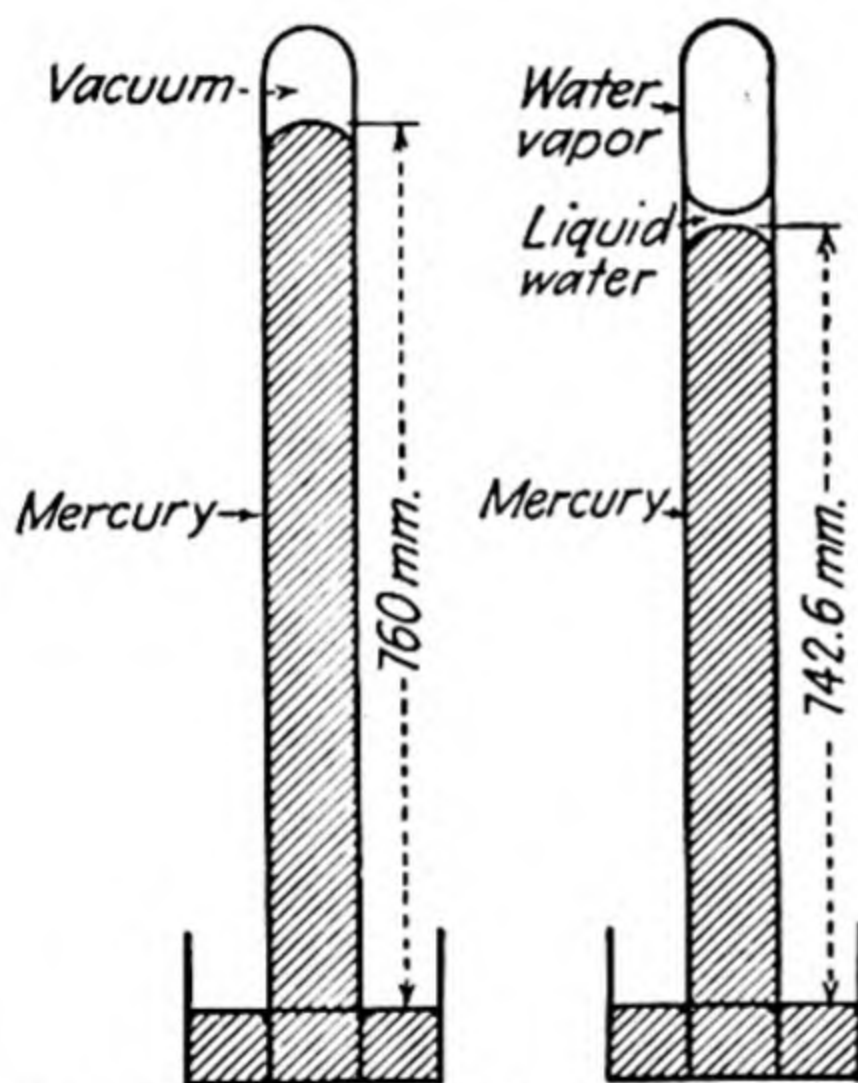
FIG. 3-1. Determination of the vapor pressure of water.

The term *vapor tension* is sometimes used in place of vapor pressure.

Vapor pressures may be measured by inserting some of the

liquid over mercury in a barometer tube. The difference in the mercury levels before and after insertion of the liquid is a measure of its vapor pressure. Figure 3-1 illustrates the determination of the vapor pressure of water at 20°C. As indicated, the vapor pressure of water at this temperature is equal to 17.4 mm. of Hg. Enough water must be added so that a few drops remain in the liquid state. This is necessary to ensure a condition of equilibrium between the liquid and its vapor. The depression of the mercury column caused by these few drops of liquid water is so slight as to be negligible save in the most exact work.

Another method for the determination of vapor pressure can be illustrated by considering the determination of the vapor pressure of mercury itself at 150°C. In this experiment 24.0 liters of dry air, at 740 mm. of Hg and 150°C., was bubbled slowly through mercury. The latter lost 0.516 g. by evaporation. It is assumed that the rate of bubbling was sufficiently slow so that the air was saturated with mercury; *i.e.*, the partial pressure of mercury vapor in the air was equal to the vapor pressure of mercury. It is also assumed that mercury vapor behaves as an ideal gas.

The number of moles of air n_1 is

$$n_1 = \frac{p_1 v}{RT} = \frac{^{740}\!/_{760} \text{ atm.} \times 24.0 \text{ liters}}{0.0821 \dfrac{\text{liter} \times \text{atm.}}{\text{mole} \times °\text{K.}} \times 423°\text{K.}} = 0.672 \text{ mole}$$

The number of moles of mercury vapor formed, n_2, is

$$n_2 = \frac{0.516 \text{ g.}}{200.6 \text{ g./mole}} = 0.00257 \text{ mole}$$

If the mixture of air and mercury vapor obeys Dalton's law, then the partial pressure of mercury vapor, which is equal to the vapor pressure of mercury, is

$$p_2 = P\left(\frac{n_2}{n_1 + n_2}\right) = 740 \text{ mm.}\left(\frac{0.00257}{0.00257 + 0.672}\right)$$
$$= 2.82 \text{ mm. of Hg}$$

As shown in Table 3-2, the vapor pressures of all liquids increase rapidly with rise in temperature. The logarithm of the vapor pressure of a liquid is approximately a linear function of the reciprocal of the absolute temperature. If the vapor pressure at some temperature is known, that at another temperature can be cal-

culated, provided that the heat of vaporization per mole of the liquid is known. The simplified equation by which this calculation is made is based upon certain approximations. These are (1) that the heat of vaporization of the liquid remains constant

TABLE 3-2. APPROXIMATE VAPOR PRESSURES OF SOME LIQUIDS AT VARIOUS TEMPERATURES

Tempera-ture, °C.	Vapor pressure, mm. Hg				
	Ethyl ether	Carbon tetra-chloride	Ethyl alcohol	Benzene	Water
0	185	32.9	12.2	25.3	4.6
35	760	176	104	149	42
77	2,720	760	690	660	314
78	2,870	800	760	710	327
80	3,023	843	813	760	355
100	4,953	1,463	1,697	1,340	760

during the temperature interval in question; (2) that the vapor of the liquid obeys the ideal-gas law; and (3) that the volume of 1 mole of liquid is negligible compared with that of 1 mole of its vapor. The resulting equation, known as the modified Clapeyron-Clausius equation, is

$$\log \frac{p_2}{p_1} = \frac{L_v}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \tag{3-1}$$

In this equation p_1 and p_2 are the vapor pressures of the liquid at the absolute temperatures T_1 and T_2, respectively, L_v is the heat of vaporization of 1 mole of the liquid, and R is the gas constant. In the equation L_v and R must be expressed in consistent units.

Vapor pressures also increase somewhat with increase of external pressure on the liquid, this external pressure having the effect of squeezing the molecules out of the liquid, causing more rapid evaporation. A simplified expression for the change of vapor pressure with change in external pressure may be derived by making certain approximations. These are, first, that the vapor obeys the ideal-gas law; and second, that the volume of 1 mole of liquid does not change appreciably with changes in external pres-

sure. The equation based on these approximations is

$$\log \frac{p_1}{p_2} = \frac{V_L(P_1 - P_2)}{2.303RT} \tag{3-2}$$

In Eq. (3-2), p_1 and p_2 are the vapor pressures corresponding to the external pressures P_1 and P_2, respectively, T is the absolute temperature, V_L is the volume of 1 mole of the liquid, and R is the gas constant. In using this equation the values of V_L, P, and R must be expressed in consistent units.

It requires large changes in external pressure to produce very small changes in vapor pressure. For example, the vapor pressure of water, at 35°C. and 1 atm. external pressure, is 42 mm. of Hg. The student can calculate, by use of Eq. (3-2), that to increase the vapor pressure of water, at 35°C., to 43 mm. of Hg, would require an increase in external pressure to over 34 atm.

The change of vapor pressure resulting from moderate changes in external pressure is so slight that it is commonly neglected. The relationship is discussed at this point because we shall wish to refer to it later, when considering the relation between vapor pressure and osmotic pressure.

Boiling Points. The temperature at which the vapor pressure of a liquid equals atmospheric pressure is called the *boiling point* of that liquid. It is obvious that the boiling point of a liquid depends, not only on the nature of the liquid, but also on the value of the atmospheric pressure at the time the boiling point is measured. The boiling point of water on top of a mountain is considerably lower than it is at sea level, because the atmospheric pressure on the mountaintop is less than it is at sea level. The temperature at which the vapor pressure of a liquid equals 760 mm. of Hg is known as the *normal boiling point* of that liquid. Unless it is definitely stated otherwise, the term "boiling point" refers to the normal value.

Freezing Points. If liquids are cooled sufficiently, they will freeze or pass into the solid state. In this state, the freedom of motion of the molecules is still more restricted than it was in the liquid condition, so that solids have a definite shape and an extremely limited tendency to flow. Solids have a measurable vapor pressure, although usually its value is very small.[1] The

[1] The vapor pressure of ice, small though it is, is sufficient to make possible the dehydration of frozen blood plasma under a vacuum.

freezing point of a liquid may be defined as the temperature at which the solid and the liquid phases of the substance are in equilibrium. Since both the solid and liquid phases have a vapor pressure, it follows that these two vapor pressures must also be equal at the freezing point, or else there would be a transfer from one state to the other through the vapor phase and equilibrium would not exist. The freezing point may, therefore, be redefined as the temperature at which the solid and liquid phases of a substance have the same vapor pressure. Since changes in external pressure affect the vapor pressure of the solid and liquid phases
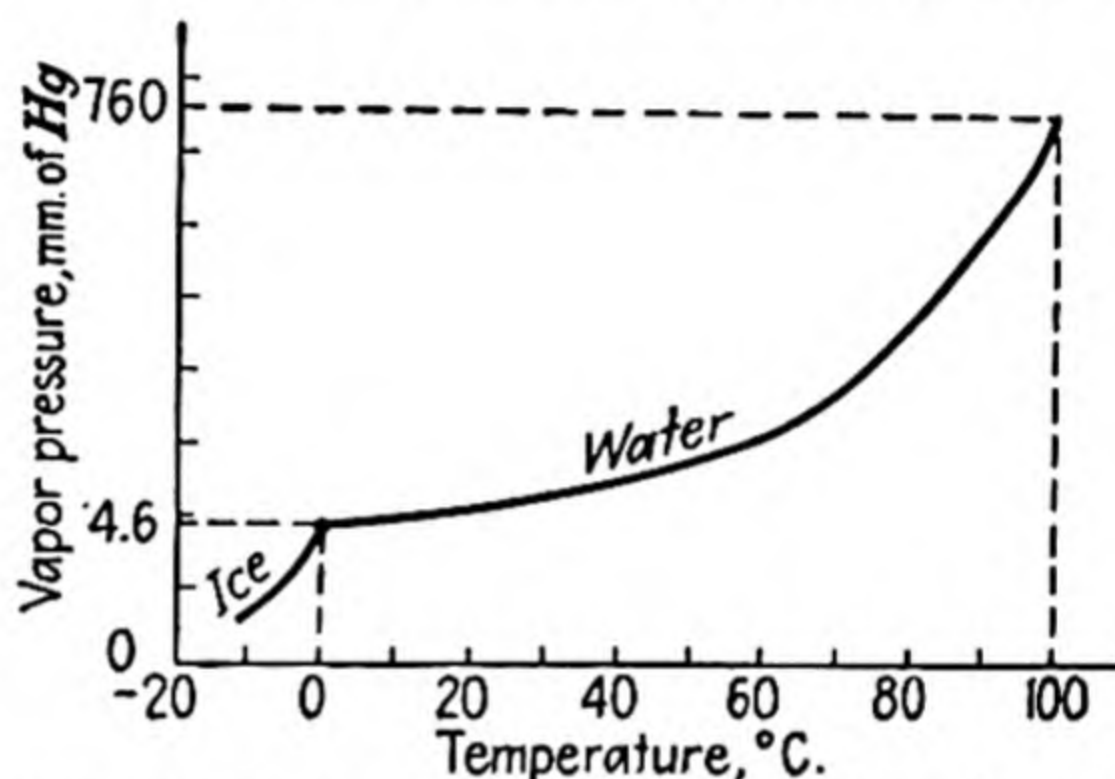
FIG. 3-2. The vapor-pressure curves for water and ice. (To conserve space, the ordinate scale is not uniform.)

unequally, and therefore change the temperature at which they are in equilibrium, the *normal freezing point* of a liquid is defined as the temperature at which both solid and liquid phases have the same vapor pressure when the total external pressure is equal to 1 atm. These definitions of normal boiling point and normal freezing point should be borne in mind when the discussion of boiling and freezing points of solutions is taken up later on (Chap. 5).

Figure 3-2 shows the vapor pressures of the solid and liquid phases of water at various temperatures, under a total external pressure of 1 atm., and shows also the normal boiling and freezing points. Increases in external pressure will affect the freezing point, raising it in the case of some liquids and lowering it in others, as, for example, water. This effect, however, is so slight for ordinary pressure changes that it is negligible in most work.

Heat of Fusion. Heat is necessary to change a substance from the solid to the liquid state, just as heat was used in changing

a substance from a liquid to a vapor. The amount of heat that is absorbed when 1 g. of a solid melts is known as the *heat of fusion* of that substance. This quantity of heat varies with the substance and the temperature. For water at 0°C., the heat of fusion is 80 cal./g. This same quantity of heat is released when 1 g. of liquid water freezes at 0°C.

Surface Tension

If 2 or 3 ml. of aniline is placed in a small bottle that is about half full of water, and a saturated solution of potassium chloride is slowly added, a point will be reached where the specific gravity of the salt solution is the same as that of aniline. The latter is then free from the action of gravity and remains suspended about halfway between the top and the bottom of the salt solution. Under these conditions, the aniline is seen to pull itself together into an almost perfect sphere, this being the form that presents the least surface for a given volume. The aniline behaves as though there were an elastic membrane over its surface. Gentle poking with a glass rod shows that this surface resists deformation. This is one manifestation of a property possessed by all liquids, known as the *surface tension* of the liquid. Other methods by which the existence of this property may be demonstrated are as follows:

1. A piece of fine copper gauze, coated with an extremely thin film of vaseline, floats on the surface of water. The water behaves as if its surface was covered by a thin membrane that supports the copper even though the latter is much more dense than water.

2. The resistance that this imaginary membrane over the surface of water offers against having a loop of thin platinum wire pulled through it is great enough to be felt by the fingers.

3. If a capillary tube, such as a piece of thermometer tubing, is inserted in a liquid, the surface of the liquid inside the capillary will be elevated, or depressed, compared with that outside, depending on whether or not the liquid wets the material of which the capillary is made. For example, water wets glass, so water rises in a glass capillary, while mercury does not wet glass, so it is depressed in a glass capillary.

4. A liquid flowing slowly from a fine tip, such as a burette tip, will form a series of drops, each drop growing in size until

its mass exerts a force just sufficient to overcome the surface tension of the liquid and rupture the surface, allowing the drop to fall.

Cause of Surface Tension. The elastic membrane mentioned in the preceding section is purely imaginary and has no actual physical existence. It is possible, however, to explain why liquids behave as if they did have such a membrane over their surface. A drop of liquid is composed of a large number of individual molecules (Fig. 3-3). It is obvious that the molecules in the interior of the drop are entirely surrounded by like molecules and therefore are attracted equally in all directions.

Vapor molecules

Liquid drop
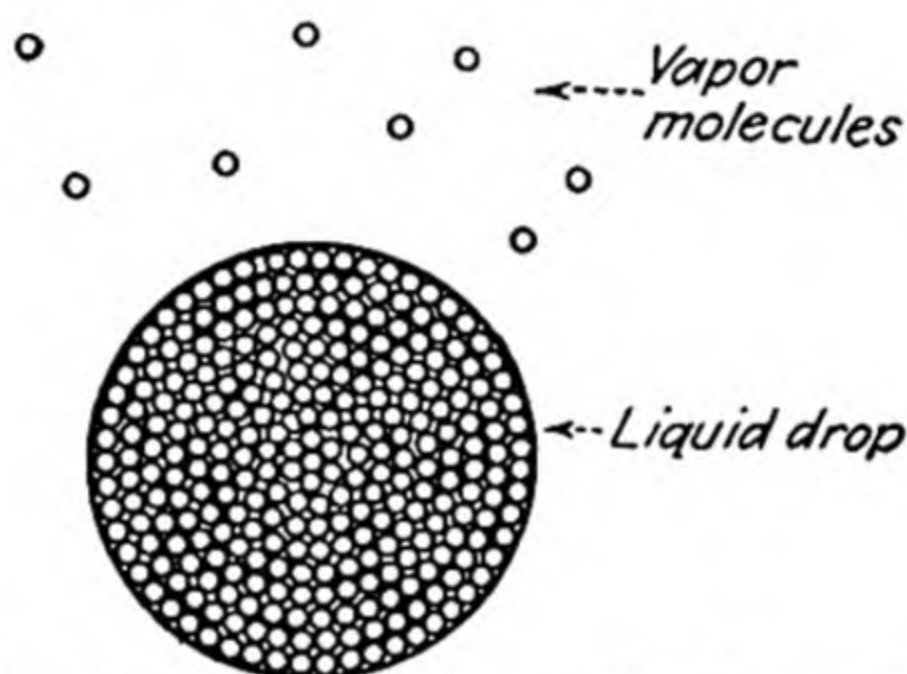
FIG. 3-3. Forces acting on the molecules in a liquid.

But those molecules in the surface are not so surrounded and are subject to an unequal force of attraction that is tending to pull them inward and make the surface as small as possible. It is this force that causes the liquid to behave as if there were a membrane over its surface which resists attempts to deform it, or to increase the extent of the surface. This force is known as the *surface tension* of the liquid. The usual symbol for surface tension is the Greek letter gamma γ.

It is apparent that if the surface is to be ruptured, or increased in extent, a force must be exerted sufficient to overcome the surface tension. The amount of this force depends on the surface tension of the liquid and also on the length of the line along which the surface is broken. Therefore, the surface tension of a liquid can be defined as the force necessary to rupture its surface along unit length. This definition suggests that the units of surface tension are either grams-weight per centimeter or dynes per centimeter.

Surface tension exists wherever two phases come into contact with each other and is sometimes known as the *interfacial tension*. The values that are ordinarily given for the surface tension of liquids refer to the tension at an interface between the liquid and air. In this case, the attraction exerted by the air molecules on the molecules in the surface of the liquid is negligible. It is also possible to measure the interfacial tension between two liquids that do not dissolve in each other. In this
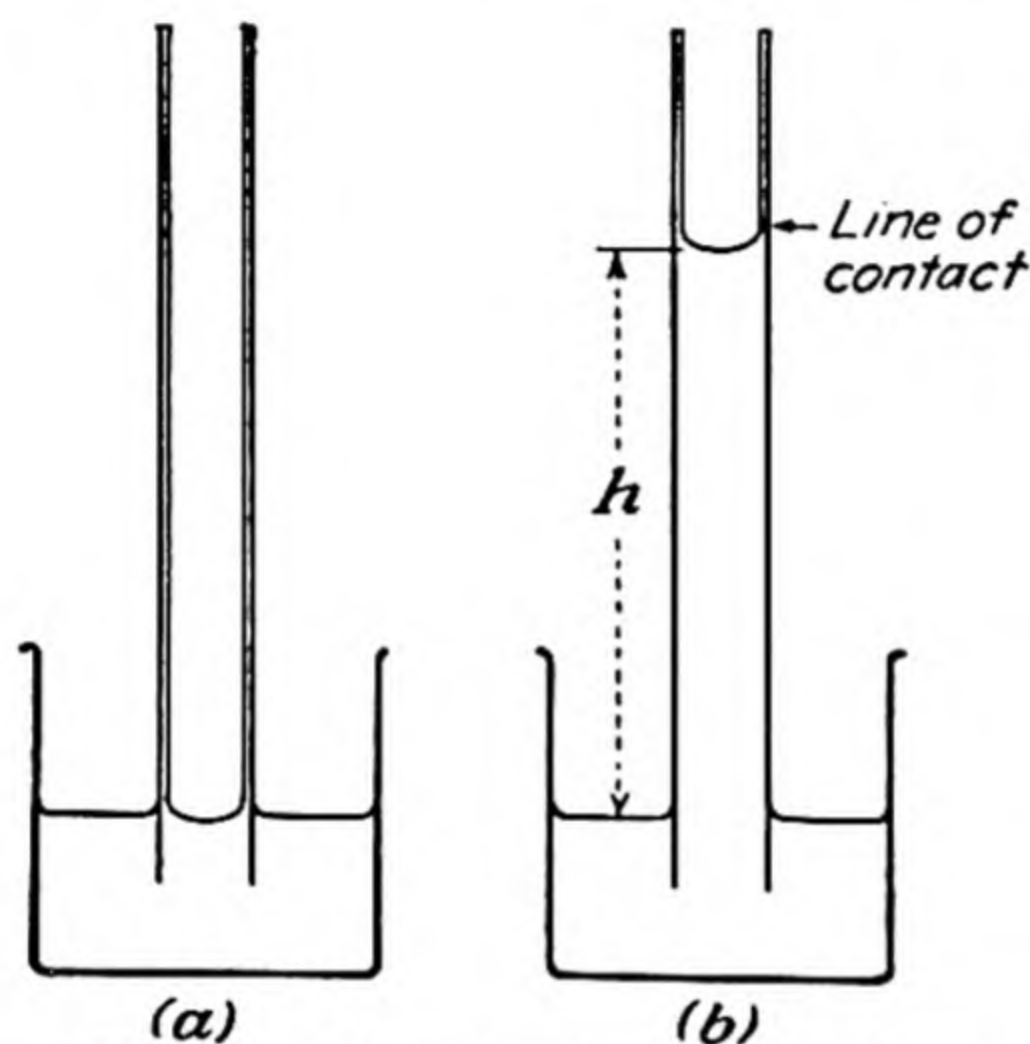

FIG. 3-4. Rise of water in a capillary.

case, the attraction of the molecules of one liquid for the molecules in the surface of the second liquid is not negligible. The interfacial tension under these conditions is determined by the difference in attractive force exerted on the surface molecules by the molecules in the interior of the two liquids. It is generally found that the interfacial tension between two liquids is less than the surface tension of that one of the two liquids having the larger surface tension.

Measurement of Surface Tension. *Capillary-rise Method.* Water molecules adhere strongly to the surface of glass, *i.e.*, the water *wets* the glass. The result is that when a glass capillary is inserted into water a thin film of water forms over the entire surface of the capillary (Fig. 3-4a). The area of this water surface compared with the volume of liquid in the capillary, is now relatively enormous. Surface tension acts to decrease this sur-

face to the smallest possible area. The film of water adheres so strongly to the glass that this film cannot be pulled down to the level of the liquid. The only other way to decrease the surface is to pull the level of the liquid up along the film. This is just what happens. The liquid level rises until the downward force exerted by gravity on the liquid just equals the upward force exerted by the surface tension. If the liquid were raised any higher, its downward pull would then be sufficient to rupture the surface at the point of greatest strain, *i.e.*, along the line around the inside circumference of the capillary where the surface of the liquid first comes in contact with the glass (Fig. 3-4*b*).

If the liquid is pulling straight down, *i.e.*, if the angle of contact[1] between liquid and glass is zero, then the amount of downward force, exerted along the line of contact, is equal to the difference between the mass of the liquid column and that of the column of air displaced by it, multiplied by the acceleration of gravity. The difference in the masses of the column of liquid and of air is equal to the volume of the liquid multiplied by the difference in the densities of liquid and of air. Therefore,

$$\text{Downward force} = \pi r^2 h (d_{\text{liq}} - d_{\text{air}}) g$$

where r is the inside radius of the capillary, h is the difference in level of the liquid surfaces inside and outside the capillary, d_{liq} and d_{air} are the densities of the liquid and air, respectively, and g is the acceleration of gravity. For ordinary work the value of d_{air} is so small that it may be neglected, and the expression becomes

$$\text{Downward force} = \pi r^2 h \, dg$$

where d refers to the density of the liquid. If r and h are expressed in centimeters, d in grams per cubic centimeter, and g in centimeters per second per second, the downward force is

[1] The angle of contact is defined as the angle formed by the solid-liquid interface and the tangent to the gas-liquid interface at the point of contact of the three phases.
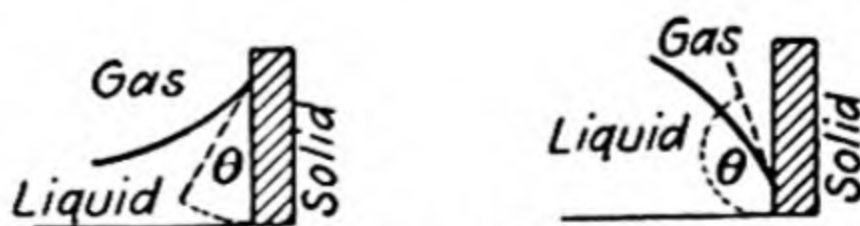
In each of the above cases θ is the angle of contact.

expressed in dynes. At equilibrium this downward pull is just balanced by the upward pull of the surface tension of the liquid along the line of contact between the liquid and the glass. This upward pull equals the surface tension multiplied by the length
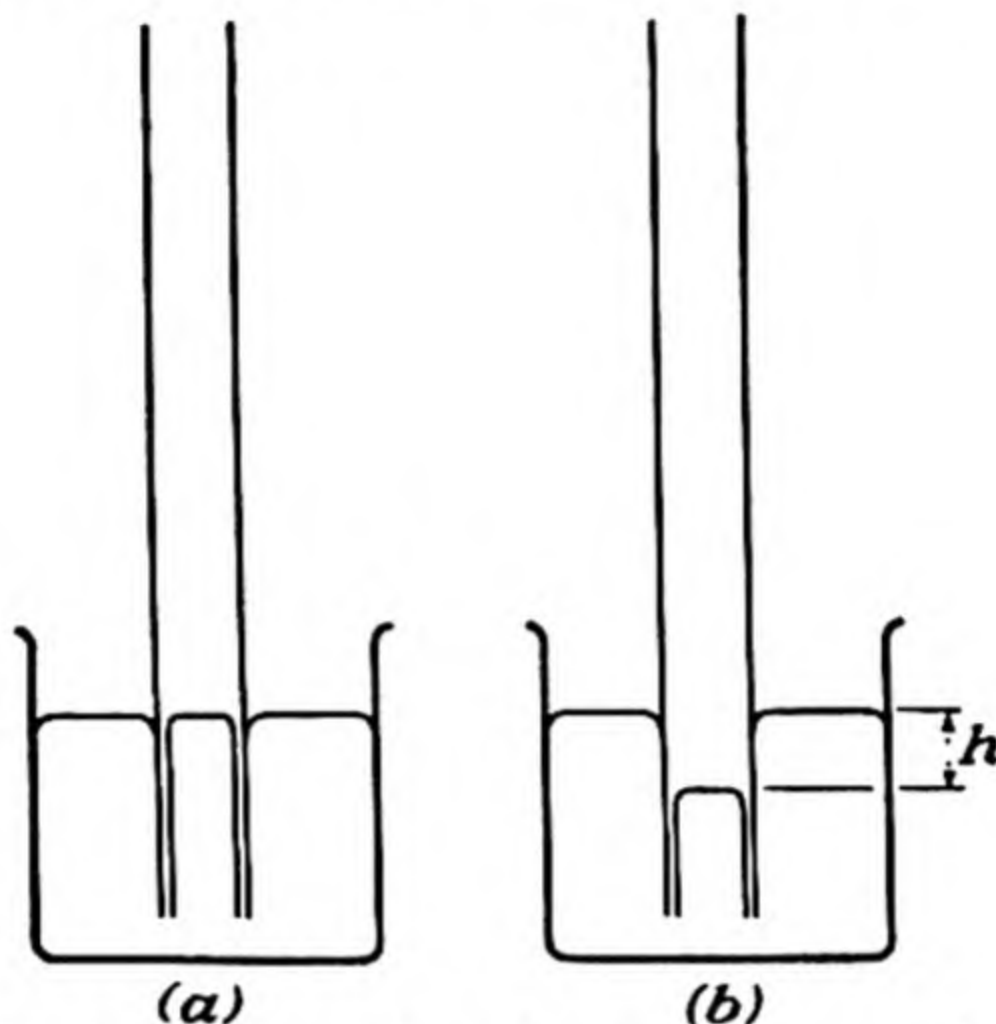

FIG. 3-5. Depression of mercury in a capillary.

of the line of contact, *i.e.*, the inside circumference of the capillary. Therefore,

$$\text{Upward pull} = 2\pi r\gamma$$

At equilibrium, therefore,

$$2\pi r\gamma = \pi r^2 h\, dg$$

or

$$\gamma = \frac{\pi r^2 h\, dg}{2\pi r} = \frac{1}{2}\, rh\, dg \text{ dynes/cm.} \tag{3-3}$$

Example. Water, at 20°C., rises 14.85 cm. in a capillary whose inside diameter is 0.200 mm. Calculate the surface tension of water, assuming that the density of water is 1.00 g./cm.³

$\gamma = \frac{1}{2}rh\, dg = \frac{1}{2} \times 0.0100 \text{ cm.} \times 14.85 \text{ cm.} \times 1.00 \text{ g./cm.}^3$

$\times 980.7 \text{ cm./sec.}^2$

$= 72.8 \text{ dynes/cm.}$

In the case of a liquid, such as mercury, which does not wet glass, the exposed surface is convex upward (Fig. 3-5a). In attempting to decrease this surface area, the surface tension will depress the level of the mercury in the capillary. At equilib-

rium the pressure of the mercury outside the capillary, tending to force the liquid up in the tube, will just equal the force exerted by surface tension to depress it (Fig. 3-5*b*). Equation (3-3) is valid for calculating surface tension in this case also.

If the liquid whose surface tension is being measured does not wet glass strongly, it may happen that the height *h* will be determined by the adhesion of liquid to glass rather than the surface tension of the liquid. In other words, the liquid will not rise in the capillary so high as it should according to its surface tension. In this case, the angle of contact will not be zero and Eq. (3-3) can be modified to give correct values for the surface tension by the introduction of cos θ.

$$\gamma = \frac{1}{2} \frac{rh\, dg}{\cos\theta} \qquad (3\text{-}4)$$

A modification of the capillary rise method which can be applied to the measurement of the interfacial tension between two immiscible liquids is illustrated in Fig. 3-6. The less dense of the two liquids, *A*, is placed in the upper vessel, the lower part of which is a capillary of radius *r*, which dips into the more dense liquid, *B*. The amount of *A* that is added is just enough to cause the interface between *A* and *B* inside the capillary to be exactly at the same level as the surface of *B* outside the capillary. The interfacial tension is then given by the expression

FIG. 3-6. The determination of the interfacial tension between two immiscible liquids.

$$\gamma_{AB} = \frac{1}{2} rh\, dg \qquad (3\text{-}5)$$

in which *h* is the difference in the levels of the surfaces of *A* and *B*, and *d* is the density of the lighter liquid, *A*.

There are other methods available for the determination of surface and interfacial tensions, but those based on the measurement of the capillary rise are considered to be the most accurate.

Factors Affecting Surface Tension. The surface tension of all liquids decreases with rise in temperature. The surface tension is also affected by dissolving various substances in the liquid. Inorganic salts have little effect on the surface tension of water, sometimes increasing it slightly Sugar has practically

no effect, but other organic substances, such as soaps, alcohols, acids, esters, and bile salts, decrease the surface tension of water to a marked degree. It is this lowering of the surface tension of water by soap that permits stretching of the surface to make possible the blowing of soap bubbles.

If some flowers of sulfur is sprinkled on the surface of water, the sulfur, although more dense than water, will be held on the surface by the surface tension. But if a soap solution, or one of the commercial wetting agents, is added, the surface tension is decreased sufficiently so that the sulfur sinks.

TABLE 3-3. SURFACE TENSION OF SOME LIQUIDS AT 20°C., IN DYNES/CM. AT THE LIQUID-AIR INTERFACE

Liquid	γ
Mercury	520
Water	72.8
Glycerin	65.2
Benzene	28.9
Ethyl alcohol	22.3
Ethyl ether	17.0

TABLE 3-4. INTERFACIAL TENSION BETWEEN SOME LIQUID PAIRS AT 20°C., IN DYNES/CM.

Interface	γ
Water–chloroform	27.7
Water–olive oil	22.9
Water–ethyl ether	9.7
Alcohol–olive oil	2.26

Surface tension may be counteracted by the presence of charged particles on the surface of the liquid, as illustrated in the following experiment. A globule of mercury is placed in a glass dish and is covered with water to which is added a drop of potassium dichromate solution and a few drops of dilute nitric acid. This solution oxidizes some of the mercury to mercurous ions, and these ions are adsorbed on the surface of the globule. These positively charged ions repel each other and thus counteract the surface tension of the mercury, so that the globule flattens and spreads out in the dish. If the mercury is now touched with a clean iron nail, the iron will reduce the mercurous ions to metallic mercury. With the disappearance of the positively charged ions, the surface tension of the mercury will once more cause it to contract. Thus the globule will shrink away from the nail, but as soon as the contact is broken, mercurous ions

are formed once more and the mercury spreads out, renewing contact with the nail. If the nail is adjusted to the correct position, the globule will pulsate for a considerable period of time.

By means of thermodynamic reasoning, which is beyond the scope of this discussion, J. Willard Gibbs established the following important rule: *Solutes that lower the surface tension of a liquid become more concentrated in the surface layer of the solution than they are in the body of it.* The reasonableness of Gibbs's conclusion may be demonstrated in the following way, provided that the reader is willing to accept the established thermodynamic fact that the energy of any system tends to reach a minimum value. The system we shall consider is a sphere of water containing a solute that lowers the surface tension. The surface of this system possesses a certain amount of surface energy which is equal to the surface tension multiplied by the area of the surface.

$$\text{Surface energy} = \frac{\text{dynes}}{\text{cm.}} \times \text{cm.}^2 = \text{ergs}$$

This surface energy may be decreased either by decreasing the surface area or by decreasing the surface tension. Since the surface area of a sphere is a minimum for a given volume, it cannot be decreased. Therefore any diminution of surface energy must result from a decrease in surface tension. In this case, this is accomplished by the movement of solute into the surface layer, giving a greater concentration there than in the main body of the sphere. In a similar way, it can be shown that those solutes that increase surface tension will become more concentrated in the interior of a solution than they are in the surface.

Applications of Surface Tension. 1. One of the reasons why soap is effective as a cleansing agent is that it lowers the interfacial tension between water and greasy substances, thus permitting the water to surround the substance and wash it away.

2. Many of the manufacturers of tooth pastes, nasal jellies, and mouth washes advertise that the efficacy of their products depends in part on the fact that they contain substances which lower the surface tension. This permits the preparation to spread evenly over the surface with which it comes in contact, allegedly increasing the efficiency of its antiseptic action.

3. Many of the substances present in the blood lower its surface tension. If, as sometimes happens, a bubble of air is introduced

into the blood stream a liquid-air interface is formed. According to Gibbs's rule the substances which lower the surface tension of blood become concentrated at this interface. If, as is the case, these substances also increase the viscosity of blood, they form a tough membrane around the air bubble which prevents its absorption. This is one of the ways by which an embolus may be produced which sometimes causes death if it reaches the pulmonary artery or the heart.

VISCOSITY

If the rates at which water and molasses flow from similar containers are compared, it is apparent that there is a great difference between the speeds at which these two liquids flow, the molasses being much slower than the water. This rate of flow is determined by the *viscosity* of the liquid.

A liquid flowing through a tube may be pictured as composed of a series of concentric cylinders. If the liquid wets the tube, that cylinder which is in contact with the wall of the tube is stationary. Each succeeding cylinder slides past the one outside it with a velocity that increases as the center of the tube is approached. A friction exists between the molecules of the liquid which resists this sliding of the cylinders. This friction is the viscosity of the liquid.

Viscosity may be measured by determining the force necessary to slide one face of a centimeter cube of a liquid past the opposite stationary

FIG. 3-7. Illustrating the definition of viscosity.

face with a velocity of 1 cm./sec. In Fig. 3-7 is represented a cube of liquid 1 cm. on a side. The viscosity of the liquid is equal to the force that must be applied to the top face of the cube, in the direction *v*, to move that face past the bottom face with a velocity of 1 cm./sec. For a body of liquid of any other dimensions, this force is directly proportional to the area of the surface moved, the velocity with which the surface is moved, and the viscosity of the liquid. It is inversely proportional to the distance that separates the two faces.
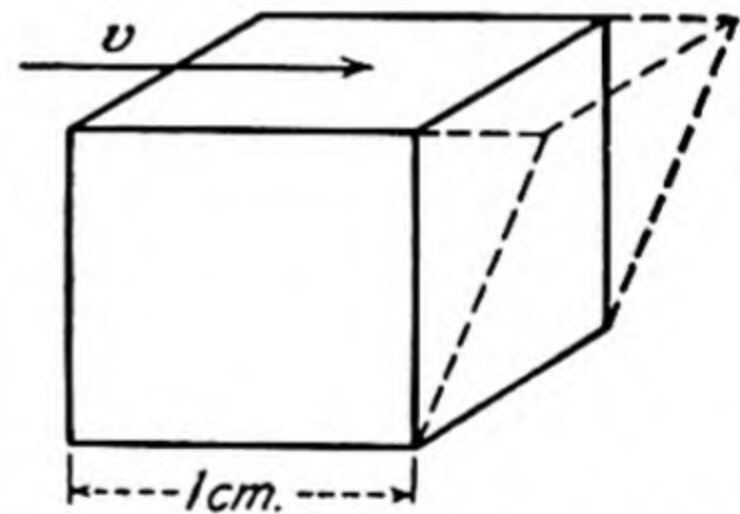
$$\text{Force} = \frac{\text{velocity} \times \text{area} \times \text{viscosity}}{\text{distance between faces}}$$

or

$$\text{Viscosity} = \frac{\text{force} \times \text{distance between faces}}{\text{velocity} \times \text{area}}$$

From this expression, the c.g.s. units in which viscosity is stated are seen to be

$$\text{Viscosity} = \frac{\text{dynes} \times \text{cm.}}{\dfrac{\text{cm.}}{\text{sec.}} \times \text{cm.}^2} = \frac{\text{dynes}}{\text{cm.}^2} \times \text{sec.} = \frac{\text{g.}}{\text{cm.} \times \text{sec.}}$$

The usual symbol for viscosity is the Greek letter eta η. The unit of viscosity is the *poise*. A liquid has a viscosity of 1 poise if a force of 1 dyne will move one face of a centimeter cube of that liquid past the opposite stationary face with a velocity of 1 cm./sec.

The name "poise," for the unit of viscosity, is obtained from the name of the French scientist Poiseuille, who derived the formula and method for measuring viscosities of liquids.

Measurement of Absolute Viscosities. Poiseuille's method for the measurement of viscosities consisted in determining the time of flow of liquids through capillaries. The data that must be obtained are

> v = volume of liquid used
> t = time of flow
> p = hydrostatic pressure on the liquid
> r = radius of capillary
> l = length of capillary

These values may be substituted in Poiseuille's formula to obtain the viscosity as follows:

$$\eta = \frac{\pi r^4 p t}{8 l v} \tag{3-6}$$

By substituting the correct units for v, t, p, r, and l, the student should show that Eq. (3-6) gives the viscosity in poises.

Measurement of Relative Viscosities. Poiseuille's method for the determination of absolute viscosity is difficult of application and is time consuming. The method ordinarily used is one devised by Ostwald, which compares the viscosity of a liquid with that of a liquid whose viscosity is known. This is done by measuring the time of flow of equal volumes of the two liquids

through the same capillary. Enough of the liquid of known viscosity (liquid *A*) is put into the apparatus (Fig. 3-8) to fill the bend in the tube. The liquid is then sucked up through the capillary until the surface of the liquid is above the upper graduation mark *a*. It is then allowed to flow down, and the time required for the meniscus to pass from the upper to the lower graduation *b* is noted. The apparatus is then thoroughly cleaned and dried, an equal volume of liquid *B* is placed in it, and the process is repeated. By using the same capillary, the values of *r*, *l*, and *v* in Poiseuille's formula are held constant. The time *t* is measured and *p*, the hydrostatic pressure, is directly proportional to the densities (d_A and d_B) of the liquids. From this it follows that

$$\frac{\eta_B}{\eta_A} = \frac{t_B \times d_B}{t_A \times d_A} \tag{3-7}$$

Water is usually taken as the reference standard for viscosities, and the ratio of the absolute viscosity of any liquid to that of water, at the same temperature, is known as the *specific viscosity* of the liquid.

Example. The absolute viscosity of water, at 20°C., is 0.01002 poise. In an Ostwald viscosimeter, 2.00 ml. of water flows out in 52.9 sec., while 2.00 ml. of chloroform flows out in 20.0 sec.

Fig. 3-8. Ostwald viscosimeter.

Density of water = 1.00 g./cm.^{3}, of chloroform = 1.49 g./cm.^{3}

Temperature of experiment = 20°C. Calculate the specific and absolute viscosities of chloroform at 20°C.

Specific viscosity

$$\frac{\eta_{CHCl_3}}{\eta_{H_2O}} = \frac{20.0 \text{ sec.} \times 1.49 \text{ g./cm.}^3}{52.9 \text{ sec.} \times 1.00 \text{ g./cm.}^3} = 0.563$$

Absolute viscosity

$$\eta_{CHCl_3} = 0.563 \times 0.01002 \text{ poise} = 0.00564 \text{ poise}$$

Factors Affecting Viscosity. For compounds belonging to the same class, we might reasonably expect viscosity to increase with increasing molecular weight. Thus, in the case of the straight-chain hydrocarbons, the viscosity should rise as the length of the chain increases. This proves to be so. In the case of compounds
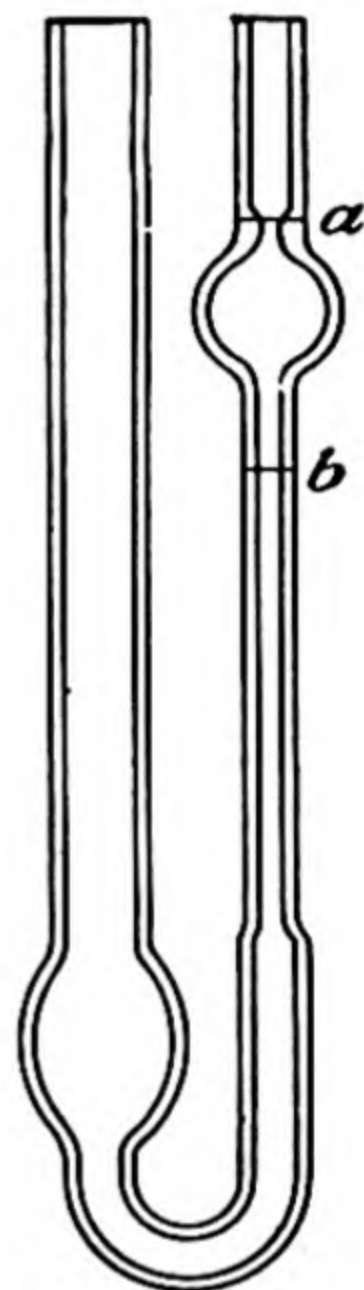
containing hydroxyl groups, there is the possibility of the formation of a bond between the hydrogen of this group on one molecule and the oxygen of this group on an adjacent molecule. (See the discussion of the hydrogen bond in Chap. 6.) This bond would increase the difficulty of moving one layer of liquid past another and, hence, would increase the viscosity. This would explain why water shows a higher viscosity than chloroform, which has a much higher molecular weight. It would also account for the high viscosity of glycerin, whose molecule contains three hydroxyl groups.

TABLE 3-5. ABSOLUTE VISCOSITIES OF SOME COMMON LIQUIDS, IN POISES, AT 20°C.

Liquid	Viscosity
Aniline	0.0440
Benzene	0.00649
Chloroform	0.00564
Ether	0.00234
Ethyl alcohol	0.01192
Glycerin	8.30
Mercury	0.0157
Castor oil	9.86

Viscosity decreases rapidly with rise in temperature. The addition of cane sugar increases the viscosity of water, but the addition of highly ionized salts decreases it. The presence of suspended matter, such as red and white corpuscles, and colloids, such as proteins, albumin, and globulin, increases the viscosity of water. Thus, water, at 37°C., has a viscosity of 0.0069 poise, while blood serum at the same temperature has a viscosity of 0.01 poise, and whole blood 0.03 poise.[1]

Applications of Viscosity. 1. In arteriosclerosis the hardening and contracting of the arterial walls decrease the diameter of the capillaries through which the blood must flow. The viscosity of the blood resists flow through these capillaries, which means that a higher pressure must be used to force it through them. This results in a condition of high blood pressure, with its accompanying strain on the heart.

[1] Not only is the viscosity of the blood affected by the concentration of red corpuscles, but it is also a function of the pressure gradient on the blood at the time of measurement. This means that viscosity may vary with the dimensions of the measuring instrument. Therefore care should be used in interpreting viscosity data on blood.

2. In fevers, a condition in which an increased circulation of the blood is desirable, a rise in body temperature decreases the viscosity of the blood by about 3 per cent per degree centigrade, thereby permitting a more rapid flow of blood without putting a correspondingly increased strain on the heart.

3. In cases of asphyxia an increase in the viscosity of the blood results from the swelling of the corpuscles, caused by an increase in the concentration of carbon dioxide in the blood. (See the discussion of the Donnan equilibrium in Chap. 12.)

Problems

1. Why cannot oxygen be kept as a liquid at room temperature in sealed steel cylinders, while ammonia can be so kept?

2. How many calories are absorbed in changing 10 g. of ice at 0°C. into 10 g. of steam at 100°C.?

3. A stoppered bottle, capacity 1.000 liter, contains, at 35°C., 100 ml. of liquid carbon tetrachloride. What weight of carbon tetrachloride vapor is also present in the bottle?

4. The atmospheric pressure on top of a mountain is equal to 710 mm. of Hg. At what temperature will benzene boil on top of the mountain?

5. If 10.0 liters of dry air, at 15°C. and 752 mm. of Hg pressure, is bubbled slowly through toluene, likewise at 15°C., the toluene loses 0.884 g. through evaporation. What is the vapor pressure of toluene at 15°C.?

6. Using Eq. (3-1) compute the vapor pressure of water at 95°C. The observed value is 633.9 mm. of Hg.

7. Acetone (density = 0.792 g./cm.^{3}) rises 60.1 mm. in a capillary whose diameter is 0.200 mm. What is the surface tension of acetone?

8. The interfacial tension between benzene and water is measured using the method illustrated in Fig. 3-6. The density of benzene is 0.879 g./cm.^{3} The diameter of the capillary is 1.00 mm. and the height h is 15.1 mm. What is the interfacial tension?

9. At 20°C., 2.00 ml. of water flows through an Ostwald viscosimeter in 48.0 sec. At the same temperature, 2.00 ml. of acetone flows through the same viscosimeter in 20.0 sec. The density of acetone is 0.792 g./cm.^{3} Calculate the specific and absolute viscosities of acetone.

CHAPTER 4

SOLUTIONS

If a teaspoonful of sugar is added to a cup of water and the mixture is stirred, the sugar gradually disappears, or dissolves in the water. Individual molecules of sugar leave the surface of the solid and diffuse throughout the liquid until in time the sugar is evenly dispersed in the whole body of water. The mixture now presents a homogeneous appearance; *i.e.*, all parts of it look the same, and the sugar is not visibly distinguishable from the water. Such a *homogeneous mixture of two or more substances* is known as a *solution*. It is supposed that in solutions the individual particles of matter present are not larger than molecular in size. A solution may also be defined as a *one-phase system of two or more components*.

Solute and Solvent. The substance that is present in smaller quantity in the solution is known as the *solute*, or that which is dissolved. That present in larger quantity is called the *solvent*, or that which does the dissolving. Ordinarily, there is no difficulty in telling which of the components of a solution is solute and which is solvent, although in the case of solutions such as alcohol and water, where either component may be present in larger quantity, the choice of terms is somewhat arbitrary.

The most familiar types of solutions are those in which the solvent is a liquid, the solute being a gas, a liquid, or a solid. It is also possible to have solutions of gases in gases, and of gases, liquids, or solids in solids. In physiological work the most important types are those in which gases, liquids, or solids are dissolved in water. We shall, in general, limit our discussion to these types.

Description of Solutions. A solution in which there is a very small amount of solute in a large amount of solvent is known as a *dilute* solution. One in which there is a comparatively large amount of solute present is called a *concentrated* solution. This classification is a rather vague one. Later there will be discussed more definite terms for expressing the composition of solutions.

The solubility of most substances in water is limited. (Alcohol is one exception, being miscible with water in all proportions.) If enough of the solute is present, the process of dissolving will proceed to a point where the number of solute molecules dissolving per second is just equaled by the number of dissolved molecules that separate from the solution into the undissolved state. This is a condition of equilibrium, and at this point apparently no further amount of solute dissolves. When such a state of equilibrium exists between undissolved solute and dissolved solute, the solution is said to be *saturated*. In order to ensure saturation, some of the undissolved solute must remain in contact with the solution. If the solution contains a smaller amount of dissolved solute than would be in equilibrium with the undissolved solute, it is said to be *unsaturated*.

In the case of some solutes, such as sodium thiosulfate, it is possible, by heating the mixture, to dissolve a large quantity of the solute in a small quantity of water. If the clear solution, saturated at this high temperature, is then cooled, out of contact with the solid solute, the solubility of the sodium thiosulfate decreases, but, in the absence of the solid phase, none of the dissolved solute crystallizes out. The solution, at the lower temperature, now contains more dissolved solute than would be in equilibrium with the solid if it were present. Such a solution is said to be *supersaturated*. The addition of a minute crystal of solid sodium thiosulfate causes the separation of the excess dissolved solute until a state of equilibrium is reached and the solution is once more simply saturated.

SOLUTIONS OF GASES IN WATER

The solubility of gases in water varies markedly with the nature of the gas (see Table 4-1). For those gases, such as oxygen, that do not react chemically with water, the solubility is low. Gases with moderate solubilities, such as carbon dioxide, or with high solubilities, such as ammonia, are found to react to some extent with the solvent.

Factors Affecting the Solubility of Gases. Henry's Law. The solubility of all gases in water decreases with rise in temperature. The solubility of all gases in water increases with rise in pressure, and, for gases with low to moderate solubilities, *i.e.*, having little or no interaction with the solvent, the relation between pressure

and solubility is expressed in Henry's law. This law states that *the mole fraction of gas in solution, at a fixed temperature, is directly proportional to the pressure of the gas.* The mole fraction of the gas is expressed as $n/(n + N)$, where n represents the number of moles of gas and N represents the number of moles of water. For gases of low or moderate solubility the value of n is so small compared with that of N that no considerable error is introduced if we neglect it in the denominator and write the expression simply as n/N. If N is held constant, n will vary directly as the

TABLE 4-1. SOLUBILITIES OF SOME GASES IN WATER AT 0°C. AND 1 ATM. PRESSURE OF THE GAS

Gas	Gas Dissolved in 1 Liter of Water, ml.
Helium............................	14.87
Hydrogen.........................	21
Nitrogen..........................	23.9
Carbon monoxide.................	35.4
Oxygen...........................	48.9
Carbon dioxide..................	1,713
Ammonia........................	1,300,000

pressure of the gas. In accordance with this modified expression, Henry's law is sometimes stated as follows: The mass of a gas that dissolves, at a fixed temperature, in a given amount of solvent is directly proportional to the pressure of the gas.

If a mixture of gases is confined over water, each gas will dissolve as if it were present alone at a pressure equal to its partial pressure in the mixture.

Henry's law is an ideal law which is followed quite satisfactorily by gases, such as hydrogen, nitrogen, and oxygen, that have low solubilities. Gases, such as carbon dioxide, with moderate solubility, show some deviations from the law. At room temperature these deviations are sufficiently small so that in the succeeding discussions we shall assume that carbon dioxide follows Henry's law. The very soluble gases, such as ammonia, show large deviations from the law. These deviations become less as the temperature is raised.

An alternative statement sometimes given for Henry's law is: The volume of a gas, measured under the experimental conditions, that dissolves in a given volume of solvent is independent of the pressure of the gas. This may be illustrated by the following

example. We shall assume that, at the temperature of the experiment, carbon dioxide obeys Henry's law and Boyle's law.

At 20°C. and 1 atm. pressure of carbon dioxide, 943 ml. of that gas dissolves in 1 liter of water. The mass of carbon dioxide dissolved is 1.7 g. At 20°C. and 2 atm. pressure of carbon dioxide, 3.4 g. of the gas dissolves in 1 liter of water. This 3.4 g. of the gas, at 2 atm. pressure, will occupy the same volume, 943 ml., that 1.7 g. of the gas occupies at 1 atm. pressure.

When a gas is confined over water, the space not only contains the gas in question but is also saturated with water vapor. Therefore, in order to determine the partial pressure of the gas, it is necessary to subtract from the total external pressure the vapor pressure of water at the temperature of the experiment.

Methods of Expressing the Solubility of Gases. There are in common use four methods for expressing the solubility of a gas in water.

1. *Mole Fraction.* The most definite, but least used, method is to state the mole fraction of the gas in the solution. According to Henry's law the mole fraction of a gas in solution is directly proportional to the pressure of the gas. Therefore, if the mole fraction of a gas in solution at one pressure is known, it is possible to calculate the mole fraction in solution at a different pressure.

Example. Calculate the mole fraction of carbon dioxide in water at 0°C. and 2 atm. pressure of carbon dioxide. Under these conditions, 6.72 g. of the gas dissolves in 1 liter of water. The number of moles of carbon dioxide is $\dfrac{6.72 \text{ g.}}{44.0 \text{ g./mole}} = 0.153$ mole. The number of moles of water is

$$\frac{1,000 \text{ g.}}{18.0 \text{ g./mole}} = 55.5 \text{ moles}$$

Therefore, the mole fraction of carbon dioxide is $\dfrac{0.153}{0.153 + 55.5} = 0.00274$. (At 0°C. and 1 atm. pressure of the gas, the mole fraction of carbon dioxide in water is 0.00137.)

Sometimes solubilities are expressed in terms of *mole per cent.*

Mole per cent = mole fraction × 100

2. *The Solubility Coefficient.* This method and the following one, the absorption coefficient, are most commonly used to express the solubility of gases. The *solubility coefficient S*
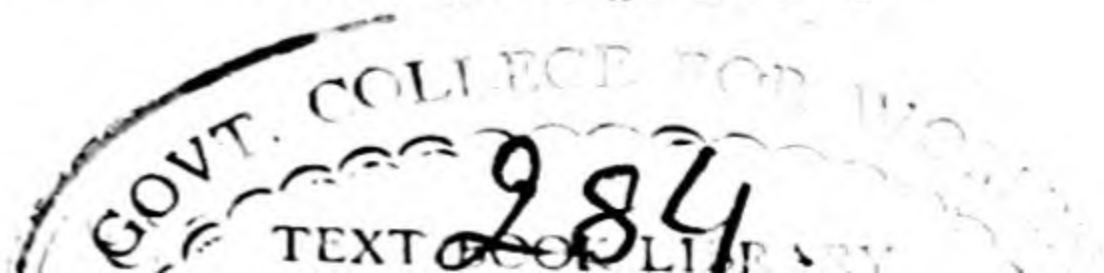
is defined as the ratio between the volume, measured at the experimental conditions, of the gas dissolved and the volume of the solvent. According to Henry's law the volume, measured at the experimental conditions, of the gas dissolved is independent of the pressure of the gas. Therefore, S is independent of the pressure. However, S does vary with the temperature, and its values at various temperatures must be determined experimentally.

TABLE 4-2. VALUES OF THE SOLUBILITY COEFFICIENT FOR CARBON DIOXIDE
AT VARIOUS TEMPERATURES

$S_{0°C.}$	1.713
$S_{10°C.}$	1.238
$S_{20°C.}$	0.943
$S_{25°C.}$	0.825
$S_{30°C.}$	0.738
$S_{40°C.}$	0.608

3. *The Bunsen Absorption Coefficient.* The Bunsen *absorption coefficient* α is defined as the ratio of the volume, reduced to standard conditions, of gas dissolved at 1 atm., to the volume of the solvent. The volume of a gas, reduced to standard conditions, is proportional to the number of moles of the gas. According to Henry's law, the number of moles of a gas dissolved is proportional to the pressure of the gas. Therefore, knowing the volume, reduced to standard conditions, of gas dissolved at 1 atm., it is possible to calculate the volume, reduced to standard conditions, dissolved at any other pressure. Values of the absorption coefficient must, however, be determined experimentally at different temperatures.

Example. At 20°C. and 1 atm. pressure of carbon dioxide, 471.5 ml. of that gas, measured under the experimental conditions, dissolves in 0.500 liter of water.

$$S_{20°C.} = \frac{0.4715 \text{ liter}}{0.500 \text{ liter}} = 0.943$$

If this same amount of gas should be reduced to standard conditions, it would occupy 471.5 ml. $\times$ 273°K./293°K. = 439 ml. Therefore,

$$\alpha_{20°C.} = \frac{0.439 \text{ liter}}{0.500 \text{ liter}} = 0.878$$

The relation between the value of the solubility coefficient and that of the absorption coefficient at the same temperature

is given by the following expressions:

$$\alpha_{T^\circ K.} = S_{T^\circ K.} \frac{273}{T} \qquad (4\text{-}1)$$

$$S_{T^\circ K.} = \alpha_{T^\circ K.} \frac{T}{273} \qquad (4\text{-}2)$$

The volume of a gas, measured under the experimental conditions, that dissolves is independent of the pressure of the gas and is given by the expression

$$V = Sv \qquad (4\text{-}3)$$

where V represents the volume of gas dissolved, S the solubility coefficient at the temperature of the experiment, and v the volume of the liquid.

TABLE 4-3. VALUES OF THE ABSORPTION COEFFICIENT FOR SOME GASES AT VARIOUS TEMPERATURES

	Carbon monoxide	Carbon dioxide	Oxygen	Nitrogen
$\alpha_{0^\circ C.}$	0.0354	1.713	0.0489	0.0239
$\alpha_{10^\circ C.}$	0.0282	1.194	0.0380	0.0196
$\alpha_{20^\circ C.}$	0.0232	0.878	0.0310	0.0164
$\alpha_{30^\circ C.}$	0.0200	0.665	0.0261	0.0138
$\alpha_{40^\circ C.}$	0.0178	0.530	0.0231	0.0118

The volume of a gas, reduced to standard conditions, that dissolves is proportional to the pressure of the gas and is given by the expression

$$V = \alpha v p \qquad (4\text{-}4)$$

where V represents the volume of gas dissolved, reduced to standard conditions, α represents the absorption coefficient at the temperature of the experiment, v the volume of the liquid, and p the pressure of the gas in atmospheres.

Example 1. What volume of carbon dioxide, measured under the experimental conditions, will dissolve in 700 ml. of water at 25°C. and 537 mm. of Hg pressure of carbon dioxide?

$$V = Sv = 0.825 \times 700 \text{ ml.} = 578 \text{ ml.}$$

Example 2. What is the value of $\alpha_{25^\circ C.}$ for carbon dioxide?

$$\alpha_{25^\circ C.} = S_{25^\circ C.} \times \frac{273}{T} = 0.825 \times \frac{273}{298} = 0.756$$

Example 3. What volume of carbon dioxide, reduced to standard conditions, will dissolve in 350 ml. of water at 25°C. and 2.00 atm. pressure of carbon dioxide?

$$V = \alpha v p = 0.756 \times 350 \text{ ml.} \times 2.00 = 529 \text{ ml.}$$

When a gas mixture is confined over water, the amount of each gas that dissolves is determined by the partial pressure of that gas in the mixture.

Example. Air is a mixture containing, by volume, 79 per cent nitrogen, 20.96 per cent oxygen, and 0.04 per cent carbon dioxide. What volume, reduced to standard conditions, of each of these gases will dissolve in 250 ml. of water from air at 20°C. and 1 atm.? (Assume that the pressure of water vapor in the air is negligible.)

$$V_{N_2} = \alpha_{20°C.} \times v \times p_{N_2} = 0.0164 \times 250 \text{ ml.} \times 0.79 = 3.2 \text{ ml.}$$
$$V_{O_2} = \alpha_{20°C.} \times v \times p_{O_2} = 0.0310 \times 250 \text{ ml.} \times 0.2096 = 1.63 \text{ ml.}$$
$$V_{CO_2} = \alpha_{20°C.} \times v \times p_{CO_2} = 0.878 \times 250 \text{ ml.} \times 0.0004 = 0.09 \text{ ml.}$$

4. *Volumes Per Cent.* This method of expressing gas solubilities is defined as the number of volumes of gas, reduced to standard conditions, that dissolves in 100 volumes of liquid at a given temperature and pressure.

$$\text{Volumes per cent} = 100\alpha p$$

Example. What is the solubility of carbon dioxide in water, in volumes per cent, at 10°C. and 1.50 atm. pressure of carbon dioxide?

$$\text{Volumes per cent} = 100\alpha_{10°C.} \times p_{CO_2} = 100 \times 1.194 \times 1.50 = 179$$

Some writers speak of the *tension* of the dissolved gas. This refers to the tendency of the gas to leave the solution. It is proportional to the concentration of the gas in the solution and is equal to the partial pressure of the gas that is in equilibrium with the solution.

Solubility of Gases in Solutions. If a gas is dissolved in water that already contains another solute, such as sodium chloride or sugar, it is found that the solubility of the gas is less in the solution than it would be in pure water. In general it can be said that, if the gas does not react chemically with the other solute, the solubility of a gas in a solution is less than it is in the pure solvent. Two theories have been advanced to explain this fact. The first theory is that the solute, such as salt or sugar, is highly hydrated, thereby decreasing the number of water molecules that are available for dissolving the gas. The second

theory is that those solutes which increase the surface tension of water tend to compress the liquid volume and, in effect, squeeze out the gas molecules. If the solute is one with which the gas reacts chemically, the solubility of the gas is increased. For example, carbon dioxide is much more soluble in a solution of sodium hydroxide than it is in pure water because the gas reacts with the solute to form sodium carbonate.

Solubility of Gases in the Blood. The most important gases in physiological work are oxygen and carbon dioxide. Animal respiration is governed by the solubility of these gases in the blood, for blood is the medium by which oxygen is carried from the lungs through the body and by which carbon dioxide is returned to the lungs and released. Blood contains, among other components, red corpuscles, the color of which is due to the presence of hemoglobin, a substance that combines chemically with oxygen. Therefore, as is to be expected, it is found that oxygen is much more soluble in blood than it is in water. If these red corpuscles are removed by centrifuging, the watery fluid that is left is known as the plasma. This contains dissolved salts whose presence decreases the solubility of oxygen. Therefore oxygen is less soluble in blood plasma than it is in pure water.

Among the substances present in the plasma are compounds that react with carbon dioxide, so it is found that that gas is more soluble in blood and in the plasma than it is in water. The solubilities of all gases in the blood increase with increasing partial pressure of the gas.[1]

Application of Gas Solubilities. When air is supplied to men working under high pressure, such as deep-sea divers or caisson workers, the solubility of the component gases in the blood is increased. If the pressure is released too suddenly, *i.e.*, if the diver is brought too rapidly to the surface, the excess gas, particularly the inert nitrogen, is released in bubbles in the capillaries of the circulatory system. These gas bubbles may rupture the capillaries or clog them, thus preventing the circulation of the blood and producing the condition known as the *bends*, which may prove fatal. To avoid this, divers are brought to the surface slowly, allowing for a gradual decrease in pressure, so that

[1] For a brief but excellent discussion of respiration, see Henderson and Haggard, "Noxious Gases," 2d ed., pp. 17–50, Reinhold Publishing Corporation, New York, 1943.

the gas is released slowly and is carried along to the lungs and exhaled without harmful effect. For the same reason caisson workers, upon returning to the surface, are placed in a decompression chamber in which the pressure is gradually lowered to that of the atmosphere.

The solubility of helium in blood is considerably less than that of nitrogen, so some success has been obtained in using mixtures of oxygen and helium in place of air for divers. The blood does not absorb so much helium as it would nitrogen, and consequently the time of decompression, or raising of the diver, is correspondingly reduced.

SOLUTIONS OF LIQUIDS IN WATER

When two liquids are shaken together, the resulting mixture falls into one of three classes: completely miscible, immiscible, or partially miscible.

1. **Completely Miscible Liquids.** Ethyl alcohol and water dissolve in each other in all proportions and are said to be completely miscible.

2. **Immiscible Liquids. Emulsions.** Benzene and water are insoluble in each other, so that mixtures of these two liquids separate into two layers with a sharp line of demarcation between them. Such liquids are said to be immiscible.

If a pair of immiscible liquids, such as olive oil and water, are shaken vigorously together, a dispersion of very fine drops of one liquid in the other will result. Such a dispersion is known as an *emulsion*. The liquid that forms the drops is known as the *disperse phase*, the *internal phase*, or the *discontinuous phase*. The other liquid is known as the *dispersion medium*, the *external phase*, or the *continuous phase*.[1] The character of such an emulsion is determined by the surface tensions of the two liquids. In the case considered, the surface tension of water is greater than that of olive oil, so that there is a greater tendency for the

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[1] The experimental determination of which one of the two liquids in an emulsion forms the internal phase and which one the external phase may be carried out as follows. On a clean glass plate put separate samples of each of the pure liquids composing the emulsion. To each sample add a drop of the emulsion. The drop will mix readily with that liquid which forms the external phase of the emulsion, but will not mix with that liquid forming the internal phase.

water to pull itself together into a spherical shape. Therefore, the water will form drops and become the disperse phase. These drops will be scattered throughout the oil, which is the dispersion medium.

The emulsion described above is only temporary. If allowed to stand it separates rapidly into two layers, one of oil and one of water. In order to make the emulsion more permanent it is necessary to add a third substance, known as an *emulsifying agent*. We shall consider two classes of emulsifying agents.

Since, in an emulsion, one liquid is dispersed in very small drops throughout the other, the interfacial area between the two liquids is large. If the interfacial tension between the two liquids is large, as is usually the case with two immiscible liquids, there is a strong tendency to decrease the interfacial area by breaking the emulsion and forming two liquid layers. This suggests that the emulsion may be made more permanent by the introduction of a third substance that will decrease the interfacial tension between the two liquids. Soap has this effect and, since it lowers the interfacial tension, it becomes concentrated at the interface and forms a film over the surface of the droplets which helps to prevent their coalescence. Another example of an emulsifying agent is egg albumin which produces the permanent emulsion of olive oil and vinegar known as mayonnaise.

Certain very finely divided, insoluble solids are also capable of acting as emulsifying agents. In order for a solid to serve in this way, it is necessary that it be wetted to a certain extent by both liquids, but much more so by one liquid than by the other. Under these conditions a greater proportion of the surface of the solid particle will be in contact with that liquid that wets it most. This will result in the liquid that wets the particle least becoming the internal phase of the emulsion. This is illustrated in Fig. 4-1, showing how soot, which is wetted more by kerosene than by water, produces an emulsion of water in kerosene.

Reversal of Emulsions. It is sometimes possible to cause the external phase of an emulsion to become its internal phase, and vice versa. Such a change is called the *reversal* of the emulsion. Among the ways in which such a reversal may be brought about is by a change in the emulsifying agent.

The character of an emulsion produced with the aid of soap is determined by the interfacial tension between each of the two

liquids and the soap film at the interface. That liquid whose interfacial tension with the soap film is the greatest will have the strongest tendency to pull itself together into drops, thus forming the internal phase. An alkali metal soap, such as sodium oleate, will cause a lower interfacial tension at a water–soap-film interface than at an olive-oil–soap-film interface. Hence, this type of soap will produce an oil-in-water emulsion. On the other hand, alkaline–earth metal soaps, such as magnesium or calcium oleates, cause a lower interfacial tension at the olive-oil–soap-film interface and will bring about a reversal of the phases, producing a water-in-oil emulsion.
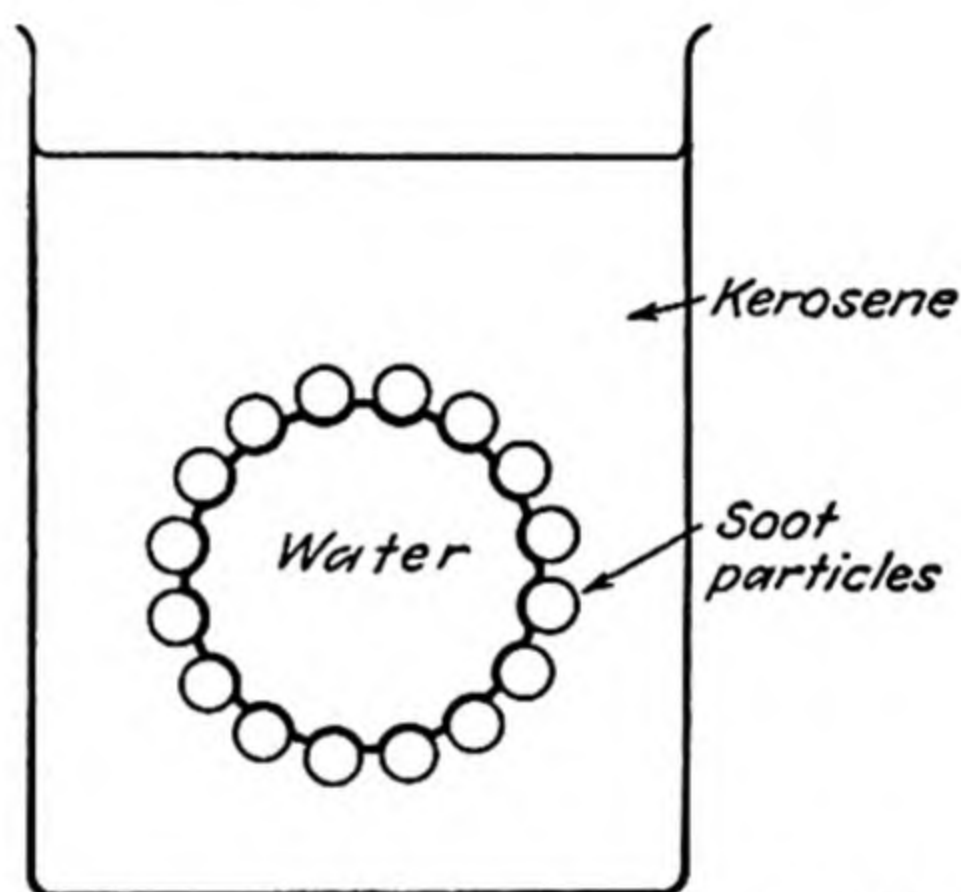
Fig. 4-1. The emulsification of kerosene and water by soot particles.

Similar reversals have been observed in the case of solid emulsifying agents. Finely divided silica is wetted more by water than by kerosene. Hence, it will produce an emulsion of kerosene in water, which is a reversal of the emulsion produced by soot.

3. **Partially Miscible Liquids.** When a small quantity of phenol is added to water at room temperature, it dissolves readily, producing a clear solution. If more phenol is added, however, a point is soon reached where the water is saturated with phenol and any additional phenol separates out into a second layer that consists of a saturated solution of water in phenol. The same thing happens if water is added to phenol. At first the water dissolves readily, but it soon saturates the phenol, and any excess water separates into a second layer that consists of a saturated solution of phenol in water. Two such liquids whose solubility in each other is limited are called partially miscible.

In Fig. 4-2 are shown the solubilities of phenol in water in the left half, and of water in phenol in the right half, determined at various temperatures. If phenol is added to water, at 20°C., it will dissolve until the composition of the solution is represented by the point *A* on the curve. This point represents the limit of solubility of phenol in water at that temperature. If more phenol is added, it separates out into a second layer, consisting of a
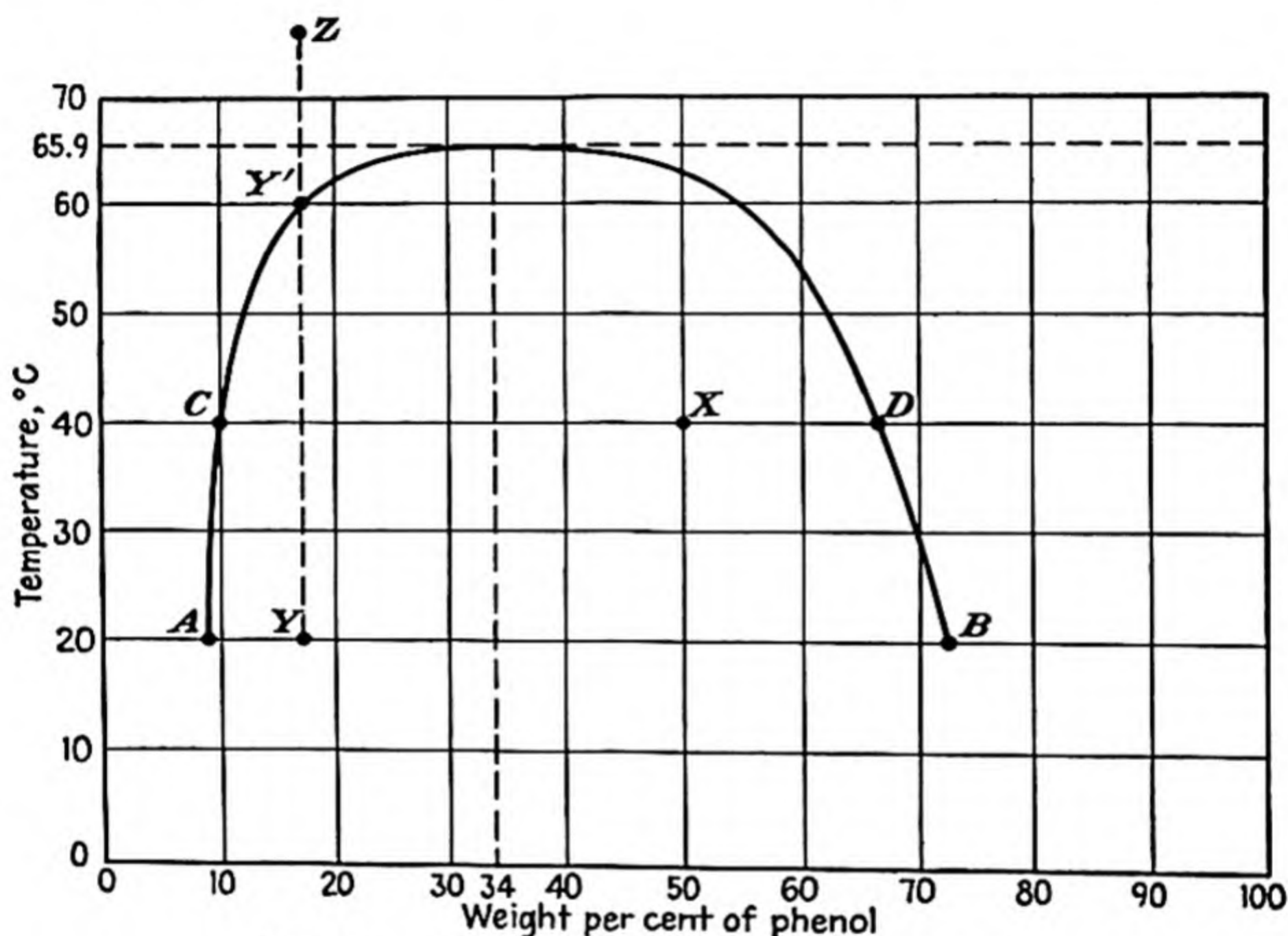
Fig. 4-2. Miscibility curve of phenol and water.

saturated solution of water in phenol, whose composition is represented by the point *B*. The same result will be obtained if water is added to phenol at 20°C. If equal quantities of water and phenol are mixed at 40°C. (point *X*), they form two layers whose compositions are represented by *C* and *D*. The relative weights of the two layers are given by the expression

$$\frac{\text{Weight of phenol-in-water layer}}{\text{Weight of water-in-phenol layer}} = \frac{XD}{CX}$$

It will be noticed that the solubilities of water in phenol and of phenol in water increase with rising temperature. The solubility curves meet each other at a maximum corresponding to the

temperature 65.9°C. Above this temperature, water and phenol are completely miscible in all proportions. This temperature is known as the *critical solution temperature* of water and phenol. The transition from partial to complete miscibility may be demonstrated as follows. Take a mixture of water and phenol, of composition represented by the point *Y*. At 20°C., this mixture consists of two layers whose compositions are represented by *A* and *B*. If the mixture is shaken, it forms a milky emulsion of one layer in the other. If this emulsion is now warmed until it reaches the temperature corresponding to *Y'* on the solubility curve, the phenol becomes completely soluble in the water and the milky emulsion changes to a clear solution. If, on the other hand, a clear solution whose composition and temperature correspond to the point *Z* is cooled, as the temperature reaches the value *Y'* the clear solution changes to a milky emulsion that gradually separates into two layers having the composition, at 20°C., represented by *A* and *B*.

Factors Affecting the Critical Solution Temperature. The addition of a third substance to a phenol–water mixture has a marked effect on the critical solution temperature. If this third substance is soluble in both the components of the mixture, the critical solution temperature is lowered. Soap has this effect, and concentrated disinfectant solutions such as phenol or cresol in water may be prepared by adding enough sodium oleate (a soap) so that the critical solution temperature is lowered below room temperature. Some of the wetting agents now on the market have a similar effect.

If the third substance is soluble in only one of the components, the critical solution temperature is raised. Sodium chloride has this effect, being soluble in water but not in phenol.

SOLUTIONS OF SOLIDS IN WATER

All solids dissolve to some extent in water, although there are wide differences in their solubility. For example, there is, on the average, less than one molecule of solute in a liter of a saturated solution of mercuric sulphide; on the other hand, 2,039 g., or about 3.6×10^{24} molecules, of sucrose dissolves in a liter of water at 20°C. The solubilities of most solids, like potassium nitrate, increase with rise in temperature. However, some, like sodium

chloride, show little change in solubility with temperature, and a few, such as calcium chromate, have solubilities that decrease with rise in temperature. Solutes, whether solids, liquids, or gases, may be divided into two main classes. Those, such as sodium chloride, whose water solutions conduct electricity are known as *electrolytes;* those, such as sugar, whose water solutions do not conduct electricity are known as *nonelectrolytes.*

METHODS OF EXPRESSING THE CONCENTRATION OF SOLUTIONS

The concentration of a solution may be expressed in various ways, some of which will be considered. It will be seen that these methods fall into one of two classes: Class I, *mass of solute in a given mass of solvent or of solution;* Class II, *mass of solute in a given volume of solution.* Each method has its advantages, but it is apparent that the first is more definite, since concentrations expressed in it are not affected by changes in temperature, while those expressed in Class II methods change as the volume of the solution changes with rise or fall of temperature.

Class I Methods. 1. *Weight Composition.* This method expresses concentration as the number of grams of solute in 1,000 g. of solvent.

2. *Per Cent by Weight.* The per cent by weight is the number of grams of solute in 100 g. of solution. Thus a 10 per cent solution of sodium chloride is prepared by dissolving 10 g. of the salt in 90 g. of water.

Sometimes a so-called 10 per cent solution is made by adding 10 g. of solute either to 100 ml. of water or to enough water to make 100 ml. of solution. The misunderstandings likely to result from such a procedure should be apparent, and the practice should be discouraged.

3. *Molality.* The molality of a solution is the number of moles of solute in 1,000 g. of solvent. The usual symbol for molality is m. All solutions of the same molality contain, in the same mass of solvent, the same number of solute molecules.

4. *Mole Fraction.* Concentrations of solutions are frequently expressed in terms of the mole fraction of the solute or solvent present. The mole fraction of the solute is $n/(n + N)$, and that of the solvent is $N/(n + N)$, where n is the number of moles of solute present and N is the number of moles of solvent.

Example. What are the mole fractions of solute and of solvent in a solution containing 200 g. of sodium hydroxide (molecular weight = 40.0) in 1,500 g. of water (molecular weight = 18.0)?

$$n = \frac{200 \text{ g.}}{40.0 \text{ g./mole}} = 5.00 \text{ moles}$$

$$N = \frac{1,500 \text{ g.}}{18.0 \text{ g./mole}} = 83.4 \text{ moles}$$

$$\text{Mole fraction of sodium hydroxide} = \frac{5.00}{5.00 + 83.4} = 0.0566$$

$$\text{Mole fraction of water} = \frac{83.4}{5.00 + 83.4} = 0.943$$

As a check on the calculations, the mole fractions of solute and solvent should add up to 1.

It will be seen in the succeeding discussions that many of the properties of aqueous solutions can be related to the mole fraction of the solute or solvent or, for dilute solutions, to the molality of the solution. Accordingly, these two methods for expressing concentrations are the ones most frequently used in physical chemistry.

5. *Mole Per Cent.* Mole per cent = mole fraction × 100.

Class II Methods. 1. The first method simply states the *number of grams of solute per liter of solution.*

2. *Molarity.* The molarity is the number of moles of solute in 1 liter of solution. The usual symbol for molarity is M. All solutions of the same molarity contain, in the same volume of solution, the same number of solute molecules.

For dilute aqueous solutions (0.1 molar or less), the difference between the values of the molarities and molalities is negligible. For more concentrated solutions or for nonaqueous solutions, the value of the molality may be calculated from that of the molarity, or vice versa, if the density of the solution is known.

Example. At 30°C. a 10.0 molal solution of sodium hydroxide has a density of 1.30 g./cm.³ What is the molarity of the solution? The solution contains 10.0 moles, or 400 g., of sodium hydroxide in 1,000 g. of water. The mass of the solution is, therefore, 1,400 g. and its volume is

$$\frac{1,400 \text{ g.}}{1.30 \text{ g./cm.}^3} = 1,080 \text{ cm.}^3$$

Each liter of the solution contains 10.0/1.08 = 9.3 moles of solute. It is, therefore, a 9.3 molar solution.

3. *Milligrams Per Cent.* Concentrations of biological solutions are quite frequently expressed in terms of milligrams per cent. This is the number of milligrams of solute in 100 ml. of solution. Thus the statement that the concentration of nonprotein nitrogen in the blood is 29.1 mg. per cent means that each 100 ml. of blood contains 0.0291 g. of nonprotein nitrogen.

4. *Normality.* The normality of a solution is the number of gram-equivalents of solute in 1 liter of solution. This method of expressing concentrations will be discussed more fully in Chap. 6.

In analytical chemistry involving chemical reactions between solutions, it is the practice to express concentrations in terms of molarities or normalities.

Changing Concentrations by Dilution. It is often found to be convenient to prepare stock solutions of reagents in a more concentrated form than needed and then to dilute them to the desired concentration before use. The method for doing this is governed by a very simple rule, which may be derived as follows. It will be remembered that Class II[1] methods tell the concentration in terms of the mass of solute in unit volume of solution. The total amount of solute present can be calculated by multiplying the concentration by the volume of the solution. The addition of water to a solution will not change the total amount of solute present; therefore, after dilution, the product of concentration and volume must be the same as it was before dilution.

$$\text{Concentration} \times \text{volume} = \text{concentration} \times \text{volume}$$
$$\text{(Before dilution)} \qquad\qquad \text{(After dilution)}$$

Concentration must be expressed in the same units on each side of the equation, and so must volume. The volume can be stated in any convenient units. Concentrations may be expressed in any Class II method and, for dilute solutions, in any Class I method.

Example 1. Given a 7 per cent solution of potassium chloride, how can 650 ml. of a 5 per cent solution be prepared? Let *x* equal the number of

[1] While this rule is strictly applicable only when the concentration is expressed in Class II methods, it may, without appreciable error, be applied when Class I methods are used, provided that the solutions are dilute.

milliliters of the 7 per cent solution required. Then

$$7\% \times x = 5\% \times 650 \text{ ml.}$$

or

$$x = \frac{5\% \times 650 \text{ ml.}}{7\%} = 465 \text{ ml.}$$

Therefore, take 465 ml. of the 7 per cent solution, and add enough water to make the total volume 650 ml.* The resulting solution will be a 5 per cent one.

Example 2. If 360 ml. of 1.7M sodium hydroxide is diluted to 500 ml., what is the concentration of the resulting solution? Let x represent the unknown concentration.

$$1.7M \times 360 \text{ ml.} = x \times 500 \text{ ml.}$$

or

$$x = \frac{1.7M \times 360 \text{ ml.}}{500 \text{ ml.}} = 1.2M$$

Preparation of Very Dilute Solutions. In making up very dilute solutions of reagents, greater accuracy may be obtained by first preparing a concentrated solution and then diluting it in steps to the desired concentration. The following example illustrates this. It is desired to prepare a solution containing 0.0050 g. of sodium chloride per liter. Let us do this in two different ways and compare the accuracy of the results. We shall assume that the limit of accuracy of the balance used is ±0.0001 g., that of the burette is ±0.01 ml., and that of the liter flask in which the solution is prepared is ±0.5 ml.

It can be shown that the error E in the final result is related to the errors e_1, e_2, e_3 of the individual steps in the preparation as follows:

$$E = \sqrt{e_1{}^2 + e_2{}^2 + e_3{}^2 + \cdots}$$

Method I.

Weigh out 0.0050 g. of sodium chloride.

$$e_1 = \pm 0.0001 \text{ g.} = 20 \text{ parts per thousand}$$

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* The volume of the final solution may be more or less than the sum of the volumes of the two liquids that are mixed because of volume changes resulting from the hydration of the solute. In this example, the volume of water to be added may be more or less than 185 ml. Therefore, the proper procedure is to place 465 ml. of the solution to be diluted in a graduate, add water to just short of the 650-ml. mark, mix thoroughly, and allow time for the solution to return to room temperature. Then add water to exactly the 650-ml. mark.

Dissolve the salt in 1 liter of water.

$$e_2 = \pm 0.5 \text{ ml.} = 0.5 \text{ part per thousand}$$
$$E = \sqrt{20^2 + 0.5^2} = 20 \text{ parts per thousand}$$

Method II.

Weigh out 0.5000 g. of sodium chloride.

$$e_1 = \pm 0.0001 \text{ g.} = 0.2 \text{ part per thousand}$$

Dissolve the salt in 1 liter of water.

$$e_2 = \pm 0.5 \text{ ml.} = 0.5 \text{ part per thousand}$$

Measure out 10 ml. of the solution formed above.

$$e_3 = \pm 0.01 \text{ ml.} = 1.0 \text{ part per thousand}$$

Dilute the 10 ml. of solution to 1 liter.

$$e_4 = \pm 0.5 \text{ ml.} = 0.5 \text{ part per thousand}$$
$$E = \sqrt{0.2^2 + 0.5^2 + 1.0^2 + 0.5^2} = 1.2 \text{ parts per thousand}$$

Note that either method furnishes a solution of the desired concentration, but that the error of the first method is about sixteen times that of the second.

DISTRIBUTION OF A SOLUTE BETWEEN TWO IMMISCIBLE SOLVENTS

When a solute is soluble in two different liquids that are immiscible, it is found that, if all three of these substances are in contact with each other, the solute will so distribute itself between the two solvents that, at equilibrium, the ratio of the mole fractions of the solute in the two solutions is a constant value, at a given temperature.[1] This statement is known as the *distribution law*. The constant referred to is known as the *distribution coefficient* of the solute between the two solvents. When the solutions are dilute, the distribution coefficient may be expressed as the ratio of the concentrations of the solute in the two solutions, and these concentrations may be expressed in any Class I or Class II method.

[1] This statement is true only when the formula of the solute is the same in the two solutions. If the solute is ionized, or is associated, in one solution and not in the other, the expression for the distribution coefficient is more complex.

For mixtures of iodine, carbon tetrachloride, and water, at 25°C., the distribution coefficient is

$$K = \frac{\text{concentration I}_2 \text{ in CCl}_4}{\text{concentration I}_2 \text{ in H}_2\text{O}} = 85$$

The value of this ratio is independent of the relative volumes of the two solvents present. The value of the ratio, however, is a constant only for dilute solutions in both solvents. If one or both of the solutions are concentrated, the value obtained for the ratio of the concentrations may differ somewhat from that of the distribution coefficient.

TABLE 4-4. VALUES OF THE DISTRIBUTION COEFFICIENTS OF SOME SOLUTES
AT 25°C.

| Solute | Solvents | | $K = \dfrac{\text{concentration in } A}{\text{concentration in } B}$ |
	A	B	
Iodine............	Carbon tetrachloride	Water	85
Iodine............	Carbon disulfide	Water	616
Iodine............	Chloroform	Water	131
Succinic acid......	Diethyl ether	Water	0.125
Bromine..........	Carbon tetrachloride	Water	30

A knowledge of the distribution coefficients is of value in problems involving the removal of a solute from solution by the addition of a second solvent.

Example. A solution contains 0.01 g. of iodine in 100 ml. of solution. This is shaken with 10 ml. of carbon tetrachloride, at 25°C. How much iodine will be extracted from the water by the carbon tetrachloride? Let x represent the number of grams of iodine removed from the water. Then at equilibrium the concentration of iodine in the water layer will be $(0.01 - x)/100$ g./ml. and the concentration of iodine in the carbon tetrachloride will be $x/10$ g./ml. Substituting these concentrations in the expression for the distribution coefficient gives

$$K = \frac{x/10}{(0.01 - x)/100} = 85$$

Solving this for x gives $x = 0.009$ g. Therefore, there will be left in the water layer only 0.001 g. of iodine.

If the process of extraction is repeated, using successive equal portions of the extracting solvent, each repetition will

remove an additional quantity of solute. The amount of solute left in the original solution following a number of such extractions may be calculated by the following equations:

Let V = volume of original solution
V' = volume of each portion of the extracting solvent
n = number of portions of extracting solvent used
w = amount of solute originally present in V
x = amount of solute left in V following n extractions

Then if the distribution coefficient is expressed as

$$K = \frac{\text{concentration of solute in extracting solvent}}{\text{concentration of solute in original solvent}}$$

the following equation is valid:

$$x = w \left(\frac{V}{KV' + V} \right)^n \tag{4-5}$$

If, on the other hand, the distribution coefficient is expressed as

$$K = \frac{\text{concentration of solute in original solvent}}{\text{concentration of solute in extracting solvent}}$$

then the equation to be used is

$$x = w \left(\frac{KV}{KV + V'} \right)^n \tag{4-6}$$

Problems

1. What is the mole fraction of hydrogen dissolved in water at 0°C. and 1 atm. pressure of hydrogen?

2. What is the value of $S_{20°C.}$ for carbon monoxide?

3. What are the values of $S_{0°C.}$ and $\alpha_{0°C.}$ for helium?

4. What volume of carbon dioxide, reduced to standard conditions, will dissolve in 400 ml. of water at 25°C. and 100 mm. of Hg pressure of carbon dioxide?

5. What volume of oxygen, measured under the experimental conditions, will dissolve in 1.500 liters of water at 30°C. and a total external pressure of 750 mm. of Hg? The vapor pressure of water at 30°C. is 31.5 mm. of Hg.

6. A mixture of oxygen and nitrogen, containing 50 per cent by volume of each gas, is confined over 600 ml. of water at 10°C. and a total external pressure of 800 mm. of Hg. What volume of each gas, reduced to standard conditions, dissolves? The vapor pressure of water at 10°C. is 9.1 mm. of Hg.

7. If the gases dissolved in Prob. 6 are completely expelled and collected dry at 18°C. and a total pressure of 1 atm., what volume will the gas mixture occupy and what will be the per cent by volume of each gas in it?

8. What is the solubility of carbon monoxide in water, in volumes per cent, at 40°C. and 2.50 atm. pressure of carbon monoxide?

9. What is the concentration of liquid water in moles per liter at 4°C.?

10. What is the concentration of liquid carbon tetrachloride in moles per liter if the density of the liquid is 1.60 g./cm.³?

11. What is the concentration, in moles per liter, of a gas at 20°C. and a pressure of 700 mm. of Hg? To do this problem, use the ideal-gas equation and solve for n/v.

12. How many grams of solute are present in 350 ml. of 0.760M barium chloride?

13. What are the molarity and molality of an aqueous solution of sulfuric acid which has a density of 1.20 g./cm.³ and contains 28 per cent by weight of sulfuric acid?

14. Calculate the weight composition and the per cent by weight of solute in a 10.0 molal aqueous solution of sodium hydroxide which has a density of 1.30 g./cm.³

15. What is the mole fraction of solute in an aqueous solution of calcium chloride which has a density of 1.29 g./cm.³ and contains 30 per cent by weight of solute?

16. What is the mole fraction of solute in a solution of iodine in carbon disulfide which has a density of 1.30 g./cm.³ and contains 6.3 per cent by weight of iodine?

17. A bottle of sulfuric acid bears on the label the following information: specific gravity = 1.5104, per cent by weight of sulfuric acid = 60.75, molecular weight of sulfuric acid = 98.08. What are the molarity and molality of the solution so described?

18. If 150 g. of silver nitrate is added to 350 g. of water at 20°C., the resulting solution has a volume of 379 ml. What are the density, molarity, and molality of the solution?

19. If 560 ml. of a 5.00 per cent solution is diluted to 750 ml. what is the concentration of the resulting solution?

20. How many milliliters of 3.20M hydrochloric acid is required to make 1.00 liter of a 2.00 molar solution?

21. A flask contains 1.80M sulfuric acid. If 50.0 ml. of this solution is withdrawn and replaced with 50.0 ml. of water, the solution in the flask is then found to be 1.60 molar. What volume of solution was originally present in the flask?

22. If 100 ml. of a water solution containing 0.0100 g. of iodine is shaken with 10 ml. of chloroform, how much iodine will be left in the water?

23. In Prob. 22 show that treatment of the water solution with two successive 5-ml. portions of chloroform will result in more complete removal of the iodine than was accomplished by the single 10-ml. portion.

24. If 300 ml. of diethyl ether containing 0.250 g. of succinic acid is shaken with four successive 10-ml. portions of water, how much succinic acid is left in the ether?

CHAPTER 5

PROPERTIES OF SOLUTIONS OF NONELECTROLYTES

Solutions of nonelectrolytes have certain properties which are related to the concentration of each of the components in the solution. If these properties of each pure component are known and if the mole fraction of each component in the solution is known, it is then possible to predict the approximate value of the corresponding property for the solution. The property of this type with which we shall be concerned is *vapor pressure*.

The partial vapor pressure of the solvent in a solution is related to the freezing-point depression and the osmotic pressure of the solution. In solutions of nonvolatile solutes, the vapor pressure of the solution is equal to the partial vapor pressure of the solvent in the solution, and this is related to the boiling-point elevation of the solution. These properties—vapor pressure, freezing-point depression, osmotic pressure, and, in the case of nonvolatile solutes, boiling-point elevation—which depend upon the number of solute molecules present and not upon their kind are known as the *colligative properties* of the solution. Measurement of any one of these properties permits calculation of the concentration of the solution and, hence, of any other of the colligative properties.

The Ideal Solution. In the discussion of gases it was found useful to establish the concept of the ideal gas, whose behavior was approached by that of actual gases as their pressure approached zero. In dealing with solutions it will likewise be useful to consider an ideal solution, whose properties are approached by those of actual solutions under certain conditions.

For our purposes we shall define an ideal solution as follows. Each component of a solution contributes something to the vapor pressure of the solution, although, in the case of nonvolatile components, the contribution may be negligible. The amount which each component contributes we shall call its *partial vapor pressure* in the solution. This is equal to the partial pressure of that same component in the vapor which is in equilibrium with the solution.

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The vapor pressure of the solution is equal to the sum of the partial vapor pressures of its components. The ideal solution may then be defined as *one in which the partial vapor pressure of each component is equal to the vapor pressure of that component in the pure state multiplied by its mole fraction in the solution.* The partial vapor pressures of the components of actual solutions approach the ideal value as the mole fraction of the component approaches unity.

Raoult's Law. The definition given above for an ideal solution may be taken as one way of stating Raoult's law, *viz., the partial vapor pressure of each component in a solution is equal to the vapor pressure of that component in the pure state multiplied by its mole fraction in the solution.* This would appear to be a reasonable conclusion, provided that the forces of attraction between dissimilar molecules in the solution do not differ from those existing between similar molecules. The vapor pressure of a component depends upon the rate at which its molecules leave the surface. This in turn depends upon the concentration of the molecules in the surface. If the addition of a second component serves simply to dilute the first component this should result in a proportionate decrease in the vapor pressure of the first component.

For a solution of two components A and B, Raoult's law may be formulated as

$$p_A = p_A^0 \frac{n_A}{n_A + n_B} \quad \text{and} \quad p_B = p_B^0 \frac{n_B}{n_A + n_B} \quad (5\text{-}1)$$

in which p_A and p_B are the partial vapor pressures of the two components in the solution, p_A^0 and p_B^0 are the vapor pressures of the two components in their pure state, and n_A and n_B are the number of moles of each component in the solution.

If one component of a solution is a solid, or a liquid with a negligible vapor pressure, it follows that the vapor pressure of the solution will be the same as the partial vapor pressure of the solvent in the solution. If the concentration of solute is low, *i.e.,* if the mole fraction of solvent approaches 1, the behavior of the solution approximates Raoult's law and

$$p = p^0 \frac{N}{n + N} \quad (5\text{-}2)$$

in which p is the vapor pressure of the solution, p^0 that of the pure solvent, n the number of moles of solute, and N the number of moles of solvent.

By subtracting each side of Eq. (5-2) from p^0 the student can derive as an alternative expression

$$p^0 - p = p^0 \frac{n}{n + N} \qquad (5\text{-}3)$$

which states that the lowering of the vapor pressure by a non-volatile solute is equal to the vapor pressure of the pure solvent multiplied by the mole fraction of the solute.

Example 1. What is the concentration of solute in an aqueous solution whose vapor pressure, at 20°C., is 17.0 mm. of Hg? The vapor pressure of water, at 20°C., is 17.4 mm. of Hg. It will be convenient to select that quantity of solution which contains 1,000 g. of water. Then

$$N = \frac{1,000 \text{ g.}}{18.0 \text{ g./mole}} = 55.5 \text{ moles}$$

Substituting these data in Eq. (5-3) gives

$$17.4 - 17.0 = 17.4 \frac{n}{n + 55.5}$$

Solving this equation gives $n = 1.3$ moles. Since this is the number of moles of solute in 1,000 g. of solvent, it follows that the concentration of the solution is 1.3 molal.

Example 2. What is the vapor pressure, at 15°C., of a solution containing 30.0 g. of urea (molecular weight $= 60.1$) in 450 g. of water? The vapor pressure of water, at 15°C., is 12.7 mm. of Hg. Substituting these data in Eq. (5-2) gives

$$p = 12.7 \frac{450/18.0}{(30.0/60.1) + (450/18.0)} = 12.5 \text{ mm. of Hg}$$

For dilute solutions the value of n is so small compared with the value of N that no considerable error is introduced if, in Eq. (5-3), $(n + N)$ is considered equal to N. Equation (5-3) would then become

$$p^0 - p = p^0 \frac{n}{N} \qquad (5\text{-}4)$$

or, stated in words, in dilute solutions of nonvolatile solutes the lowering of the vapor pressure is directly proportional to the molal concentration of the solute.

Boiling Points and Freezing Points. In Fig. 5-1 are reproduced the vapor-pressure curves of water and ice already given in Fig. 3-2. To these is added the dotted line showing the vapor pressure of a 1 molal solution of a nonvolatile solute in water. As predicted by Raoult's law, this vapor pressure is in all cases less than that of pure water at the same temperature. The boiling point has been defined as the temperature at which vapor pressure equals 760 mm. of Hg, and it is seen that this temperature is 0.51°C. higher for the solution than it is for pure water. When the solution freezes, the solid that separates is pure ice.
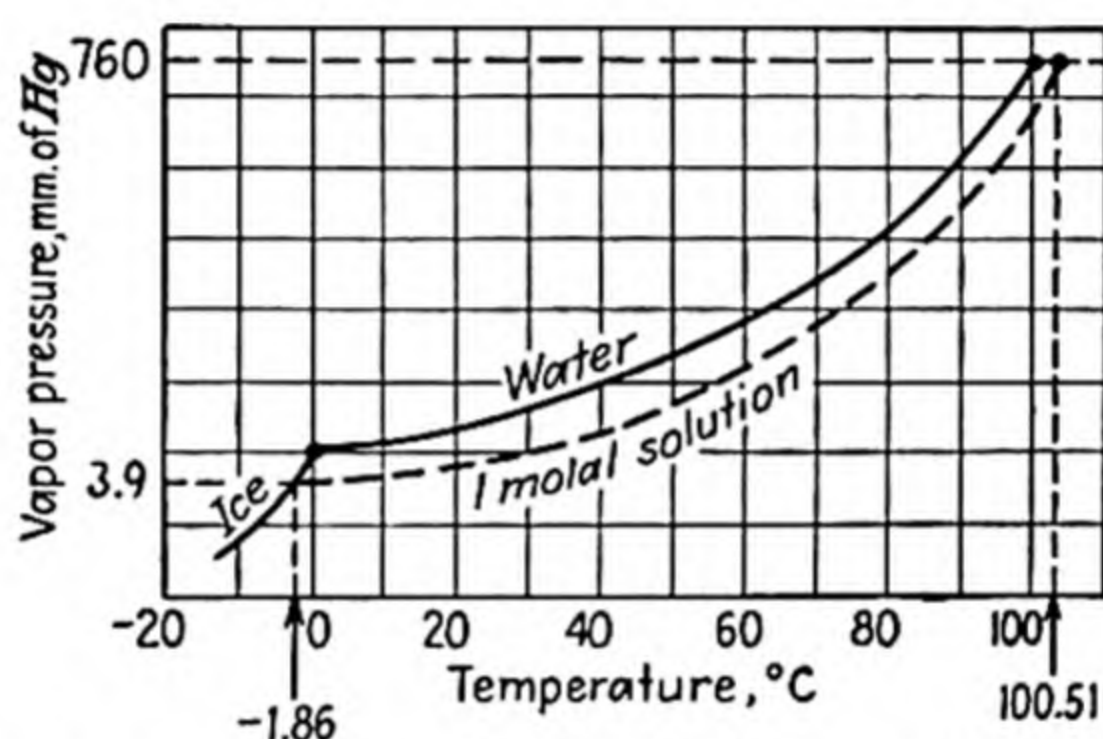
FIG. 5-1. Vapor-pressure curves for ice, for water, and for a molal solution. (To conserve space, the ordinate scale is not uniform.)

The freezing point has been defined as the temperature at which the solid and liquid forms of a substance have the same vapor pressure; therefore, the freezing point of this solution is the temperature at which the vapor-pressure curve of the solution intersects that of ice. This temperature is 1.86°C. below the freezing point of pure water. At this temperature the vapor pressure of ice is the same as the partial vapor pressure of water in a 1 molal solution, *viz.*, 3.9 mm. of Hg.

It has already been shown that all solutions in water of nonvolatile solutes of the same molal concentration show the same lowering of the vapor pressure. It follows, therefore, that all molal aqueous solutions of nonvolatile solutes will show the same boiling-point elevation (+0.51°C.) and the same freezing-point depression (−1.86°C.). These values are known as the *molal boiling-point elevation* and *molal freezing-point depression* for

water.[1] For solutions that are sufficiently dilute so that Eq. (5-4) is applicable, the boiling-point elevations and freezing-point depressions are directly proportional to the molal concentration of the solute. This makes it possible to determine the concentration of a solution of a nonvolatile solute by measuring its boiling point or its freezing point.

It is worth noting at this point that solutions of volatile solutes, for example, ethyl alcohol, in water show the same regularity of freezing-point depression. This is so because the *freezing point* of the solution is determined by the partial vapor pressure of the *solvent alone* in the solution. On the other hand, the *boiling point* of the solution is determined by the vapor pressure of the *solution*. The vapor pressure of the solution is the sum of the partial vapor pressures of the two components in the solution. As we shall see, in the case of volatile solutes this frequently results in a boiling point for the solution lower than that for the pure solvent. In any case the boiling-point change is not a colligative property when the solute is volatile.

Example 1. What is the molality of an aqueous solution that boils at 100.40°C.? Let x equal the molality.

$$\frac{x \text{ molal}}{1.00 \text{ molal}} = \frac{\text{boiling point raised } 0.40°C.}{\text{boiling point raised } 0.51°C.}$$
$$x = 0.78 \text{ molal}$$

Example 2. What is the freezing point of a solution containing 45 g. of urea in 500 g. of water? The molecular weight of urea is 60.1. Let x represent the depression of the freezing point. This solution contains 90 g. of urea in 1,000 g. of water and is, therefore, a 1.5 molal solution.

$$\frac{1.5 \text{ molal}}{1.00 \text{ molal}} = \frac{\text{freezing point depressed } x°C.}{\text{freezing point depressed } 1.86°C.}$$
$$x = 2.8°C.$$

Therefore, the solution freezes at $-2.8°C.$

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[1] Actually the values cited are the limiting values which the expressions $\frac{\text{(boiling-point elevation)}}{\text{molality}}$ and $\frac{\text{(freezing-point depression)}}{\text{molality}}$ approach as the molality approaches zero. For purposes of simplicity we have assumed that they are valid when $m = 1$.

Example 3. A solution containing 17.1 g. of sucrose in 200 g. of water freezes at −0.465°C. What is the molecular weight of sucrose? Let x represent the molality of the solution.

$$\frac{x \text{ molal}}{1.00 \text{ molal}} = \frac{\text{freezing point depressed } 0.465°\text{C.}}{\text{freezing point depressed } 1.86°\text{C.}}$$
$$x = 0.250$$

Therefore, in each 1,000 g. of water there is 0.250 mole of sucrose. But this solution contains 85.5 g. of sucrose in each 1,000 g. of water; therefore, 85.5 g. = 0.250 mole, or 1 mole = 342 g., and the molecular weight of sucrose is 342.

For determining the concentrations of physiological solutions, the boiling-point-elevation method is unsuitable because the high temperature destroys the contents of the solution. The method commonly used, therefore, is the freezing-point-depression, or *cryoscopic*, method. Since a change of 0.01 unit in molal concentration produces a change of only 0.0186°C. in the freezing-point depression, it is necessary, for work of any accuracy, to employ a very sensitive thermometer. The one commonly used in cryoscopic work is the Beckmann thermometer, which is graduated to 0.01°C. and may be read to 0.001°C.

TABLE 5-1. MOLAL BOILING-POINT ELEVATIONS AND MOLAL FREEZING-POINT DEPRESSIONS FOR SOME SOLVENTS, IN °C.

Solvent	Boiling point	Molal elevation	Freezing point	Molal depression
Water..................	100.00	0.51	0.00	1.86
Benzene...............	80.2	2.5	5.4	5.1
Chloroform.............	60.2	3.6	−63.0	4.7
Phenol.................	181.4	3.6	42.5	7.3
Ethyl alcohol............	78.4	1.2	−114.0	

Solutions in solvents other than water show the same regularity of behavior, but each solvent has its own characteristic molal elevation of the boiling point and depression of the freezing point.

Many of the substances present in the body fluids have large molecular weights (hemoglobin has a molecular weight estimated to be 67,000) or are present as colloidal aggregates of great size. In such cases, even the most concentrated solutions of these substances have such a small molality that the freezing-point depression produced is less than the experimental error involved in making the determination. Therefore,

attempts to determine the molecular weights of such solutes by the cryoscopic method have not been successful. Svedberg[1] has been successful in determining the molecular weight of hemoglobin and similar substances by photographing the distribution of their molecules in the enhanced gravitational field produced by an ultracentrifuge.

VAPOR PRESSURES AND BOILING POINTS OF MIXTURES OF LIQUIDS

1. Immiscible Liquids. When two immiscible liquids such as benzene and water are mixed together, each behaves independently of the other and shows the same vapor pressure that

Vapor-pressure curve
Temperature constant at 69°C.

Boiling-point curve
Pressure constant at 760 mm. of Hg
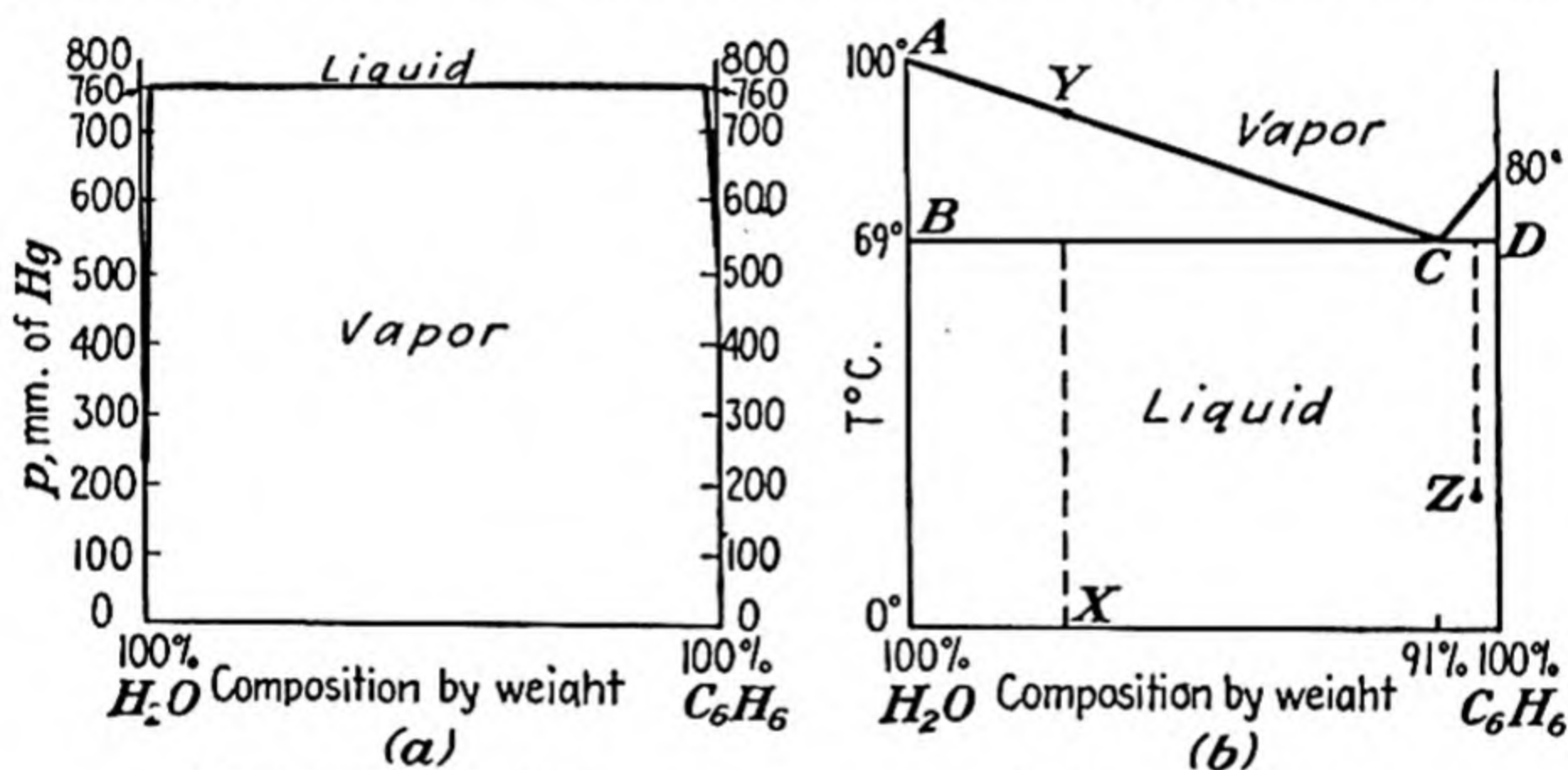
FIG. 5-2. Vapor-pressure and boiling-point curves for mixtures of water and benzene.

it would show if present alone. From this it follows that, if the mixture is stirred so that there is some of each component present in the surface, the vapor pressure of the mixture is equal to the sum of the vapor pressures of the two pure components. At a constant temperature, the value of this vapor pressure will remain constant so long as any appreciable quantity of each of the liquid components is present. Figure 5-2a shows the vapor-pressure–composition curve for benzene and water at 69°C.

The boiling point of a mixture of two immiscible liquids is the temperature at which the sum of their vapor pressures equals

[1] *Ind. Eng. Chem., Anal. Ed.,* **10,** 113 (1938). This article is a review by Svedberg of his own work.

760 mm. of Hg. This boiling point may be determined graphically by plotting the sum of the vapor pressures of the two pure components against the temperature and finding where the curve so formed crosses the 760-mm. line. The boiling point of the mixture will be less than the boiling point of either pure component and will remain constant so long as appreciable quantities of each component are present in the liquid state.

Figure 5-2*b* shows the temperature-composition, or boiling-point, curve for benzene and water under a constant pressure of 760 mm. of Hg. Let us consider what happens when a mixture of benzene and water is heated. If we start with a mixture whose composition is represented by the point X and raise its temperature, its vapor pressure will increase until, at 69°C., the vapor pressure equals 760 mm. of Hg and the mixture boils. The boiling point remains constant until one or the other of the liquid components is gone. The vapor given off from this boiling mixture will have the composition represented by the point C. The value of this composition may be calculated as follows. Since, as the liquid boils, equilibrium is maintained between the components in the vapor state and in the liquid state, it follows that the partial pressure of benzene in the vapor must be equal to the vapor pressure of liquid benzene, and similarly for water. Therefore,

$$\frac{\text{Partial pressure of benzene vapor}}{\text{Partial pressure of water vapor}} = \frac{\text{vapor pressure of liquid benzene}}{\text{vapor pressure of liquid water}}$$

We have seen, in the discussion of Dalton's law, that the partial pressure of a gas in a mixture of gases is equal to the total pressure multiplied by the mole fraction of the gas in the mixture. From this it follows that, in the vapor,

$$\text{Mole fraction of benzene} = \frac{\text{vapor pressure of benzene}}{\text{vapor pressure of mixture}}$$

The relative number of moles of benzene and water in the vapor is given by the expression

$$\frac{\text{Moles of benzene}}{\text{Moles of water}} = \frac{\text{vapor pressure of benzene}}{\text{vapor pressure of water}}$$

The relative weights of the two components in the vapor may be found by multiplying the number of moles of each by its molecular weight.

$$\frac{\text{Weight of benzene}}{\text{Weight of water}} = \frac{\text{moles of benzene} \times 78.1}{\text{moles of water} \times 18.0}$$

The relative volumes of the two components in the liquid distillate formed by condensing the vapor may be found by dividing the weight of each component by its density in the liquid state.

In the case under consideration, at 69°C., the vapor pressure of benzene is 537 mm. of Hg; that of water is 223 mm. of Hg. The mole fraction of benzene in the vapor is

$$\frac{537}{537 + 223} = 0.707$$

The relative number of moles of each component in the vapor is

$$\frac{\text{Moles of benzene}}{\text{Moles of water}} = \frac{537}{223} = \frac{2.41}{1.00}$$

The relative weight of each component in the vapor is

$$\frac{\text{Weight of benzene}}{\text{Weight of water}} = \frac{2.41 \times 78.1}{1.00 \times 18.0} = \frac{10.4}{1.00}$$

The vapor contains about 91 per cent by weight of benzene.

The density of liquid benzene is 0.879 g./cm.^{3} Accordingly, if the vapor from the boiling mixture is condensed, the relative volumes of the two components in the liquid distillate will be

$$\frac{\text{Volume of benzene}}{\text{Volume of water}} = \frac{10.4/0.879}{1.00/1.00} = \frac{11.8}{1.00}$$

The distillate contains about 92 per cent by volume of benzene.

Since, in this case, the vapor is richer in benzene than is the liquid, as the liquid boils its composition will change along the line *BC* toward *B*, but the composition of the vapor will remain constant at *C* so long as appreciable quantities of each component are present in the liquid state. As the last traces of benzene leave the liquid, the temperature will rise along the line *BA* and pure water will evaporate. If the vapor has been kept in contact with the liquid, the composition of the vapor will now move along the

line CA until the point Y is reached, at which time all the liquid should be evaporated.

The student should outline similarly the course of events when a mixture whose composition corresponds to point Z is boiled.

This behavior of immiscible liquids makes possible the extremely useful process of *steam distillation*. Suppose that we have a sample of impure chlorobenzene (boiling point = 132°C.) containing a nonvolatile impurity and that it is desired to separate the chlorobenzene from the impurity. Suppose further that it is undesirable to attempt this separation by heating the mixture up to its boiling point and distilling the solvent. We may accomplish the separation by running steam at 100°C. into the solution. The first portion of the steam run in will condense, forming the immiscible system chlorobenzene-water. The temperature of this system will rise until it reaches approximately 91°C. At this temperature the vapor pressure of chlorobenzene is 214 mm. of Hg; that of water is 546 mm. of Hg. Therefore, the mixture will boil at this temperature, and the composition of the distillate may be calculated as follows:

$$\text{Mole fraction of chlorobenzene} = \frac{214}{760} = 0.282$$

$$\frac{\text{Moles of chlorobenzene}}{\text{Moles of water}} = \frac{214}{546} = \frac{0.392}{1.00}$$

$$\frac{\text{Weight of chlorobenzene}}{\text{Weight of water}} = \frac{0.392 \times 112.56}{1.00 \times 18.0} = \frac{2.45}{1.00}$$

The density of chlorobenzene is 1.11 g./cm.^{3} Therefore,

$$\frac{\text{Volume of chlorobenzene}}{\text{Volume of water}} = \frac{2.45/1.11}{1.00/1.00} = \frac{2.21}{1.00}$$

In other words, the distillate contains more than two parts by volume of chlorobenzene to one of water and is now free from the original impurity. Since the chlorobenzene and water are immiscible, they may be separated easily in a separatory funnel.

2. **Miscible Liquids.** When a solution is composed of two liquids that are miscible, the vapor pressure of each liquid component in the solution is lowered by the presence of the other. The vapor pressure of the solution is the sum of these lowered vapor pressures of the two components in the solution. This

relation may be shown graphically by plotting the vapor pressure of the solution against its composition. For an ideal solution the plot so obtained is a straight line connecting the vapor pressures of the two pure components. This is illustrated in Fig. 5-3, which is drawn for the ideal solution of two liquid components, *A* and *B*. At 20°C. the vapor pressure of pure *A* is 40 mm. of Hg; that of pure *B* is 70 mm. of Hg. When the vapor pressure of the solution is plotted against the mole per cent of component
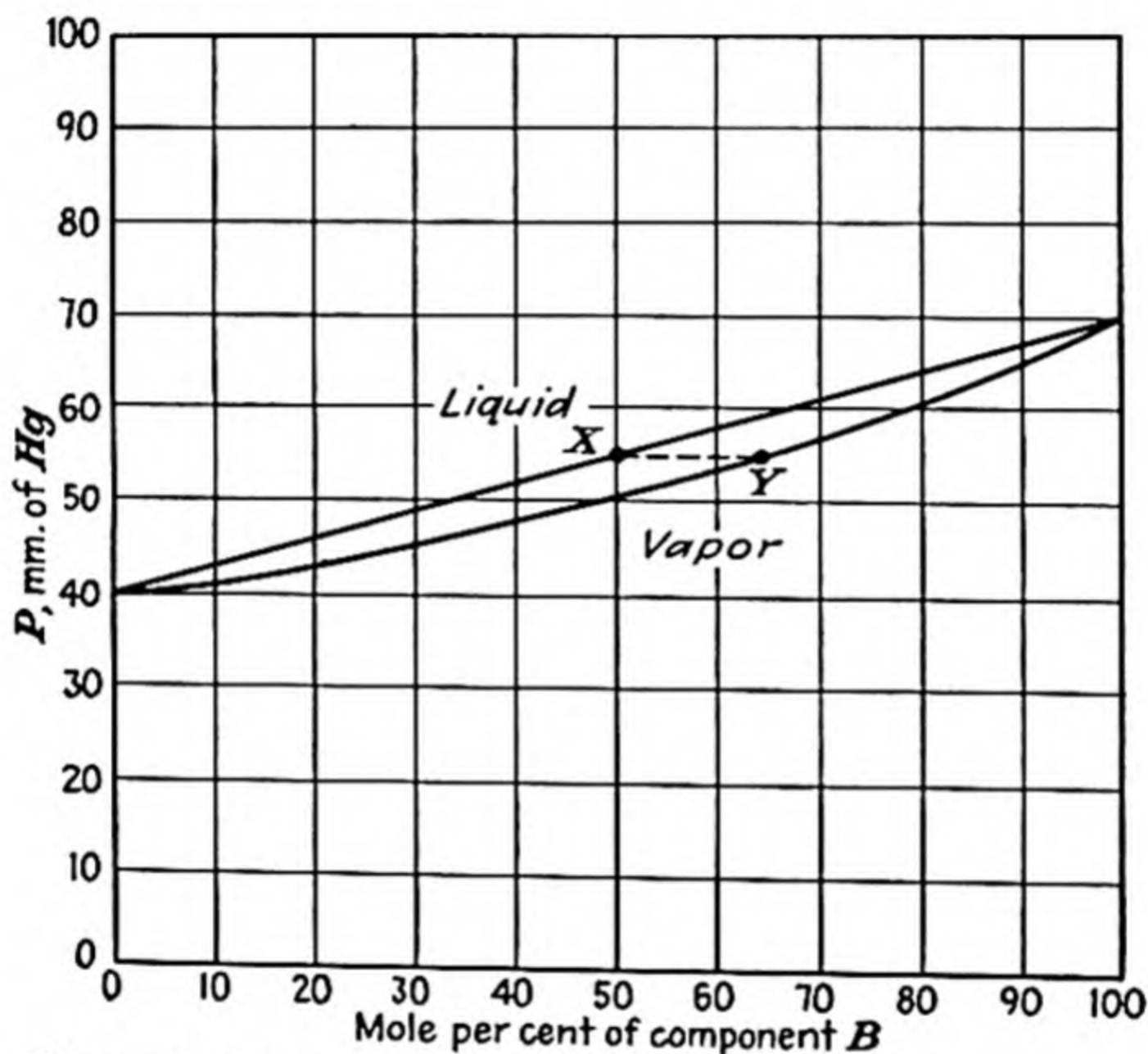
Fig. 5-3. The vapor-pressure curve for an ideal solution of components *A* and *B*. Temperature constant at 20°C.

B the straight line labeled *Liquid* is obtained. The curve labeled *Vapor* is obtained by plotting the pressure of the vapor against the mole per cent of component *B* in the vapor.

The way in which the values of the points along each curve can be calculated can be shown in the following example. The point *X* corresponds to a solution containing 50 mole per cent of each component. If the solution obeys Raoult's law, the partial vapor pressure of *A* in the solution will be 20 mm. of Hg, and that of *B* will be 35 mm. of Hg. The vapor pressure of the solution will be 55 mm. of Hg. A horizontal line drawn through point *X* intersects the vapor curve at point *Y*, which shows the composi-

tion of the vapor in equilibrium with the liquid having the composition corresponding to X. The mole fraction of B in the vapor at point Y can be calculated, assuming that the vapor obeys Dalton's law, by dividing the partial pressure of B by the total pressure of the vapor. Hence, the mole fraction of $B = {}^{35}\!/_{55} = 0.64$, or there is 64 mole per cent of B in the vapor at point Y.
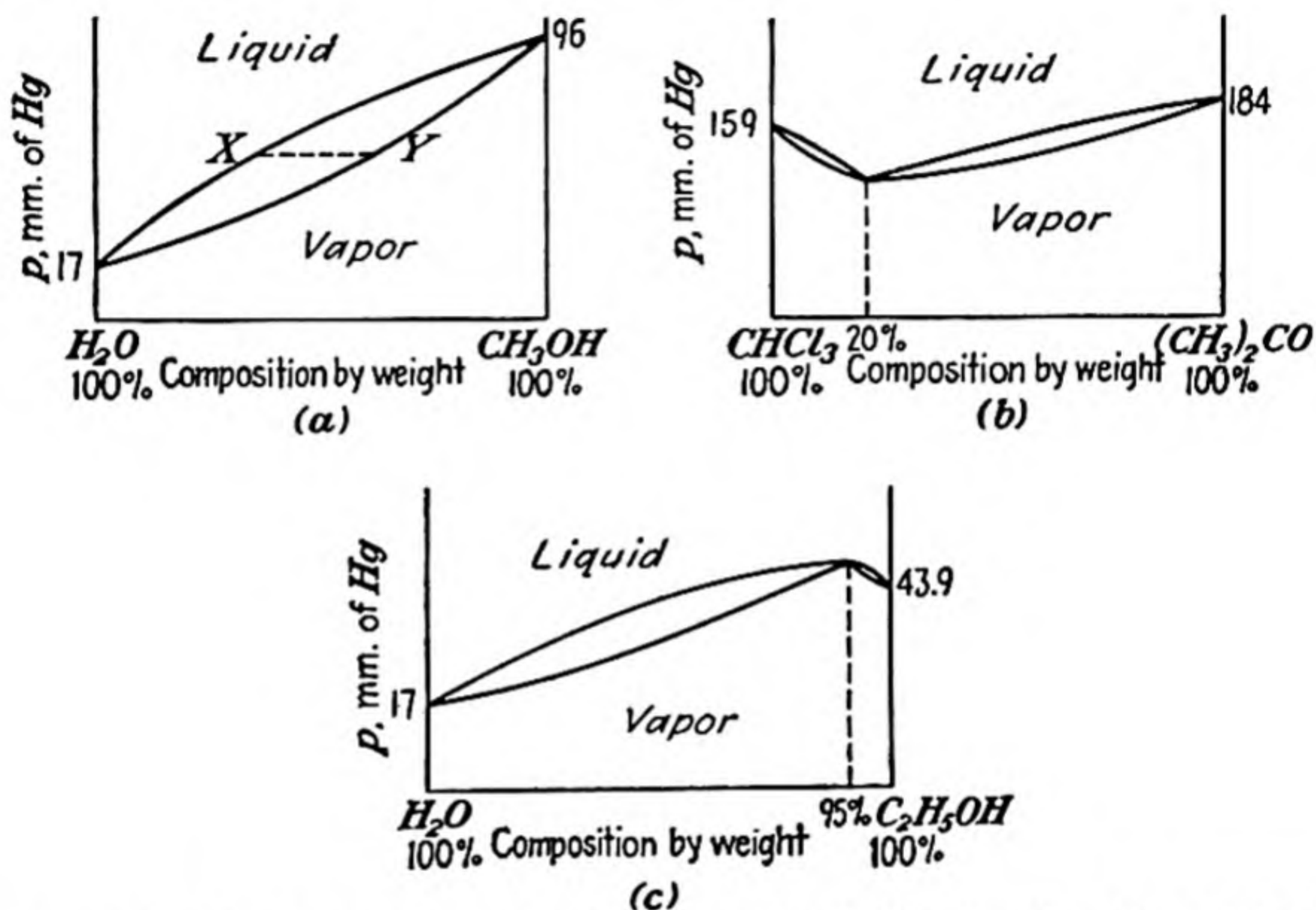
Fig. 5-4. Vapor-pressure curves for pairs of miscible liquids. Temperature constant at 20°C.

The preceding example illustrates a general rule applicable to all solutions: *The vapor in equilibrium with the solution is richer than the liquid in that component which has the higher vapor pressure.*

The vapor-pressure curves for actual solutions differ from that for the ideal solution. If the attraction between dissimilar molecules in the solution does not differ much from the attraction between similar molecules, the solution will obey Raoult's law approximately and the vapor-pressure curve will approximate that for the ideal solution. Such a solution is one in which the components are water and methyl alcohol, for which the vapor-pressure curve is given in Fig. 5-4a.

If the attraction between dissimilar molecules is greater than that between similar molecules the partial vapor pressure of each

component in the solution will be less than that computed from Raoult's law. In this case the vapor-pressure curve may show a minimum, as illustrated in Fig. 5-4*b* for mixtures of chloroform and acetone.

If the attraction between dissimilar molecules is less than that between similar molecules the partial vapor pressure of each component in the solution will be greater than that calculated
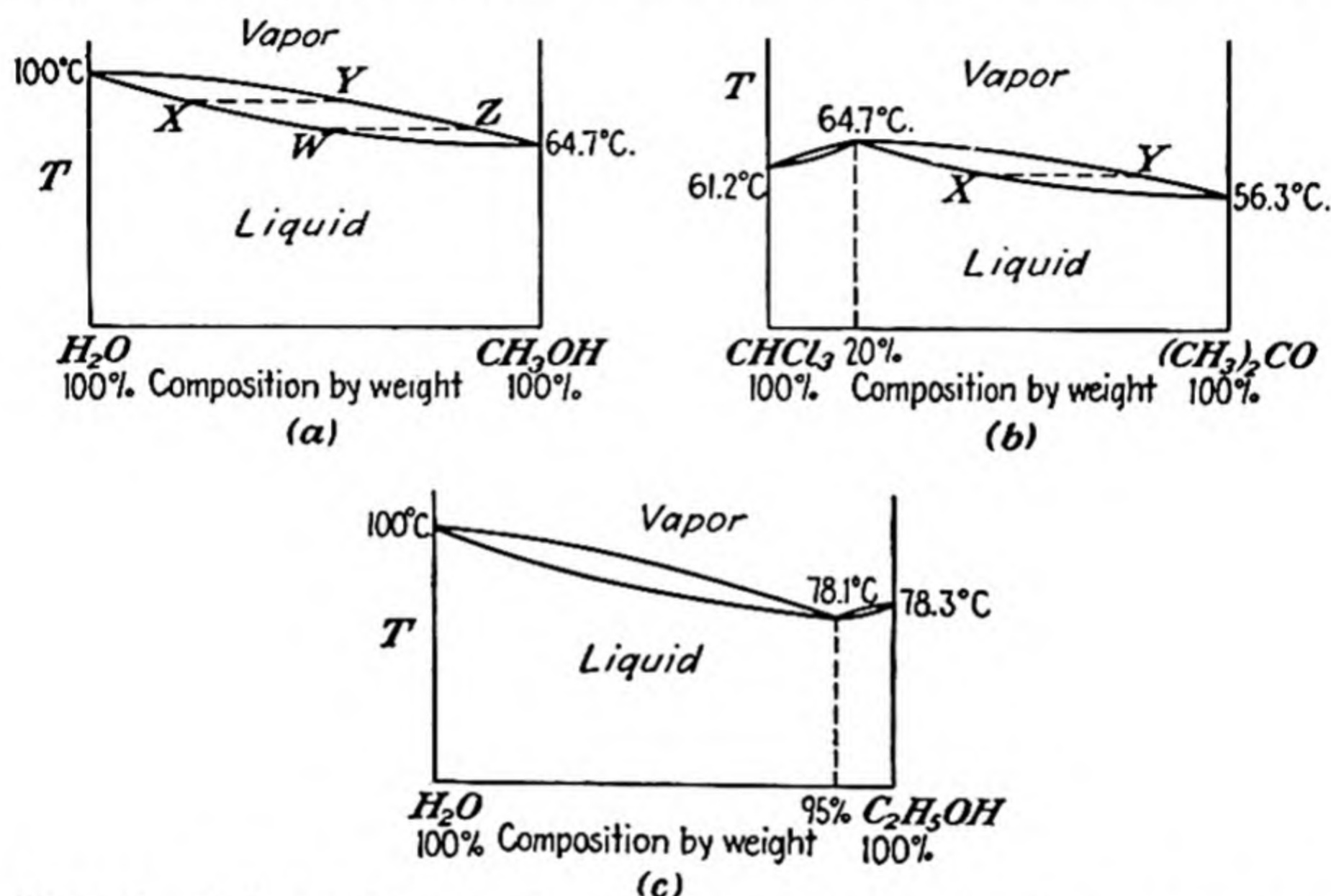
FIG. 5-5. Boiling-point curves for pairs of miscible liquids. Pressure constant at 760 mm. of Hg.

from Raoult's law. In this case the vapor-pressure curve may show a maximum, as illustrated in Fig. 5-4*c* for mixtures of water and ethyl alcohol.

Figure 5-5 shows the boiling-point-composition curves for the same liquid pairs used in Fig. 5-4. In these, the lower curve shows the composition of the liquid while the upper curve shows the composition of the vapor. It should be noted that the vapor in equilibrium with the liquid is richer than the liquid in that component having the lower boiling point.

It will be of interest to trace the course of events when each of these liquid mixtures is distilled in the usual fashion, *i.e.*, by continuously removing and condensing the vapor so that it does not remain in contact with the liquid. If a mixture of water and

methyl alcohol whose composition is indicated by point X in Fig. 5-5a is so distilled, the vapor first coming off will have the composition indicated by point Y. Since this is richer in alcohol than is the liquid, the composition of the liquid will move to the left along the curve and the boiling point will rise, reaching 100°C. as the last drop of liquid distills.

If a mixture of chloroform and acetone of composition X (Fig. 5-5b) is distilled, the vapor will have the composition Y, and the composition of the liquid will move to the left, accompanied by a rise in boiling point until the temperature 64.7°C. is reached. At this point the vapor will have the same composition as the liquid, and therefore the latter will boil without change in composition or boiling point until it is all gone.

If a mixture of water and ethyl alcohol (Fig. 5-5c) having the composition corresponding exactly to the minimum-boiling mixture is distilled, the vapor will have the same composition as the liquid, and therefore the liquid will boil without change in composition or temperature. If, however, the original composition of the liquid lies to one side or the other of this minimum-boiling mixture, then distillation will be accompanied by a rise in temperature and a variation in composition of the liquid, approaching either pure water or pure alcohol.

Fractional Distillation. By a modified method of distillation, it is possible to separate a mixture of two miscible liquids into one or the other (and, in some cases, both) of the pure components. Such a procedure is known as *fractional distillation.*

Consider a mixture of water and methyl alcohol having the composition indicated by W in Fig. 5-5a. If this is distilled until the temperature rises to X and if the distillate is collected, it will have a composition represented by some point between Y and Z. This fraction is richer in methyl alcohol than was the original liquid. A redistillation of this distillate and the collection of a new fraction will result in a further enrichment of the distillate in alcohol. If this process is repeated a sufficient number of times with proper recombination and redistilling of the fractions, practically pure alcohol can be obtained as the distillate, with practically pure water as the residual liquid.

Devices known as *fractionating columns*, in which this process of collection and redistillation of fractions is carried out automatically, are widely used in laboratory and industrial chemistry.

The principle upon which the fractionating column operates may be explained with reference to Fig. 5-6, which is a schematic representation of one type of such column known as a *bubble-cap tower*.
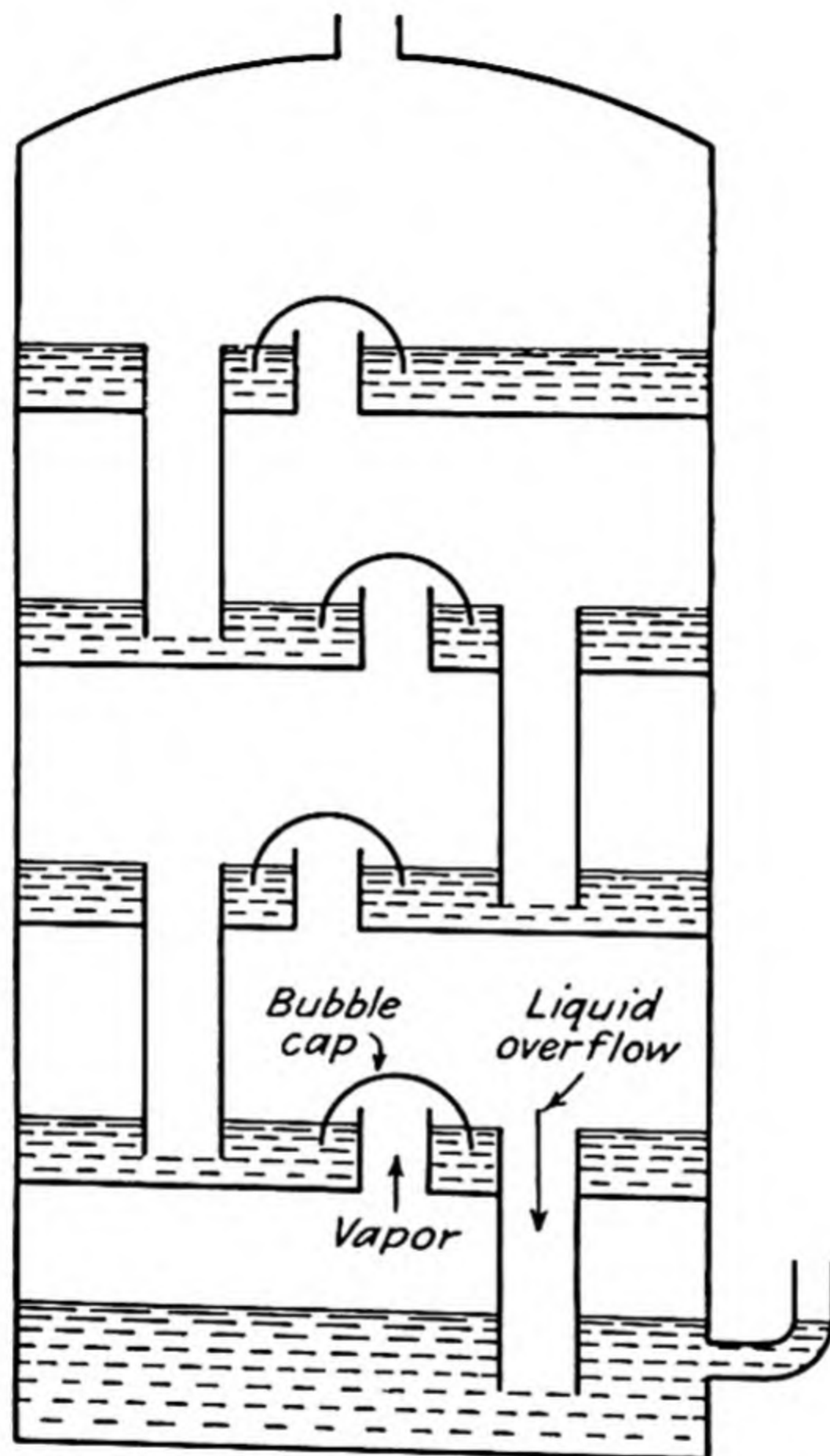
Fig. 5-6.   Bubble-cap fractionating column.

The liquid mixture to be distilled is introduced into the bottom of the tower, where it can be heated until it boils.   Above this are a series of shallow trays so provided with openings that the vapor from each tray is compelled to bubble through the liquid in the tray above it, while the condensed liquid in each tray overflows into the tray below it.

The vapor from the boiling liquid in the bottom of the tower will be richer than the liquid in that component which has the

higher vapor pressure. Consequently, the liquid that condenses in the tray above will likewise be richer than the original liquid in that component. The vapor from this tray will be still richer in the more volatile component.

This enrichment of the vapor in the more volatile component increases with each tray through which the vapor is bubbled. At the same time the overflow liquid becomes richer in the less volatile component with each tray through which it passes on its way down the tower. If there is a sufficient number of trays, it is possible to effect practically complete separation of the two components of a solution which does not show a maximum or a minimum boiling point. The vapor of the more volatile component is drawn off at the top of the tower, while the liquid form of the less volatile component accumulates at the bottom.

In actual practice, for continuous distillation, it is found more effective if the incoming liquid is fed into the tower near its middle.

In the case of mixtures of chloroform and acetone, or of water and ethyl alcohol, it is possible, by fractional distillation, to effect a separation into one or the other of the two pure components, depending upon the composition of the original liquid. But the other product will be the constant-boiling mixture. Thus any attempts to obtain pure ethyl alcohol by fractional distillation, at atmospheric pressure, from water mixtures containing less than 95 per cent alcohol will result in the separation of the constant-boiling mixture containing 95 per cent alcohol. Pure ethyl alcohol may be obtained by removal of the water by a chemical agent, such as calcium oxide, or by distillation at sufficiently low pressure, since the composition of the constant-boiling mixture changes with changes in external pressure.

OSMOTIC PRESSURE

When a solute is placed in contact with water, the molecules of the solute, as they dissolve, diffuse out through the solvent. At the same time, water molecules diffuse in among the solute molecules. This diffusion of solute and solvent continues until a condition of equilibrium is attained, at which time both solvent and solute are evenly distributed throughout the whole solution. The diffusion of the solute molecules is readily observed if a colored solute, such as potassium permanganate

is placed in contact with water. The diffusion of water molecules is not so easily observable because of their lack of color, but if the motion of the solute molecules is restricted, it is then possible to observe the effects produced by the diffusion of the solvent molecules.

Osmosis. The effect of the diffusion of water molecules can be demonstrated by use of the apparatus shown in Fig. 5-7. This apparatus consists of a vertical glass tube to the lower end of which is attached a sac made of collodion or of parchment. The
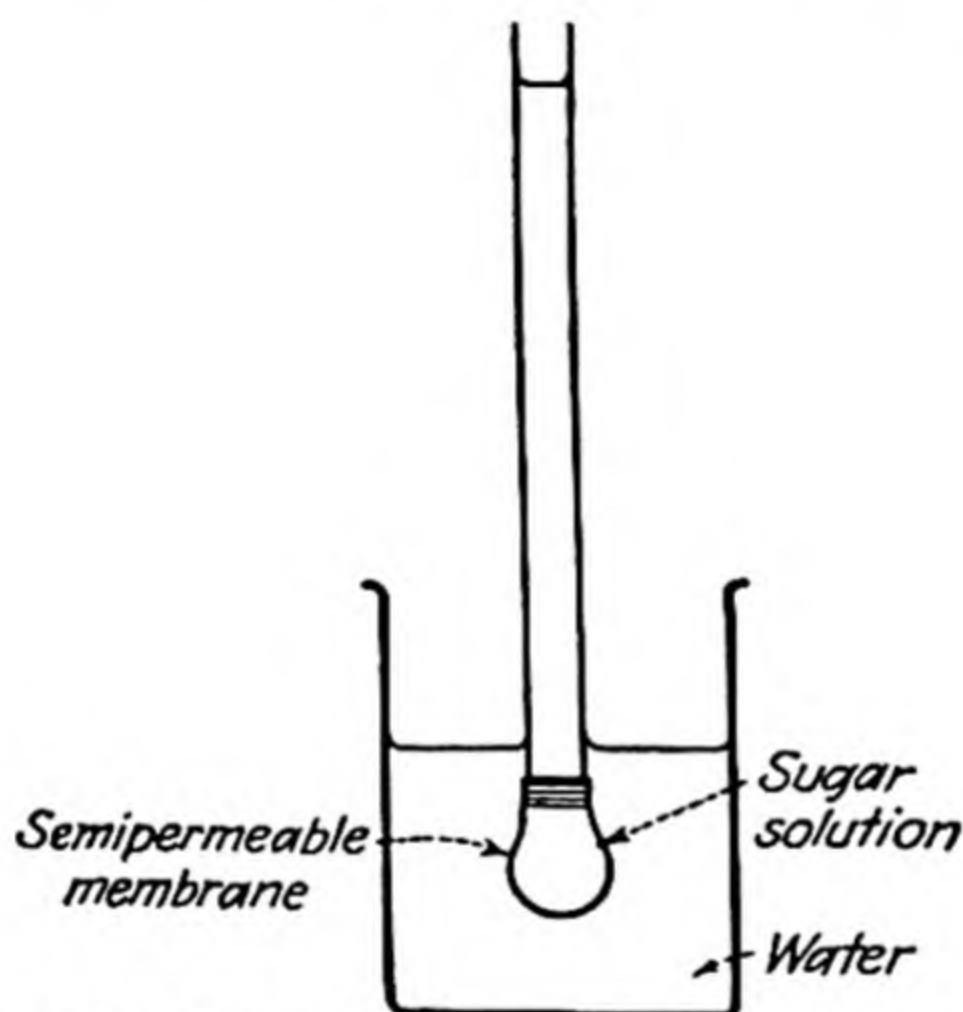
FIG. 5-7. Apparatus for demonstrating osmosis.

sac is filled with a solution of sugar in water and is then immersed in pure water. The walls of the sac form a semipermeable membrane, *i.e.*, they permit the passage of water molecules but prevent the passage of sugar molecules. The concentration of water molecules outside the sac is greater than it is inside, and consequently water will diffuse through the membrane from outside to inside in an attempt to equalize these concentrations. This motion of the water molecules is evidenced by an increase in the volume of the solution inside the sac, as shown by the rise of liquid in the vertical tube. This passage of solvent molecules across a semipermeable membrane from a region of high solvent concentration (low solute concentration) to one of low solvent concentration (high solute concentration) is known as *osmosis*.

Osmosis may take place not only between pure solvent and a

solution, but also between two solutions of differing concentrations, the flow of solvent being from the solution of low solute concentration to that of high solute concentration. If two solutions are of the same concentration so that no osmosis takes place between them, they are said to be *isosmotic*.

Osmotic Pressure. Osmosis continues until equilibrium is established between the solvent inside and outside the membrane, *i.e.*, until the same number of solvent molecules per second is passing through the membrane in each direction. This condition of equilibrium may be reached in two different ways.

1. If the concentration of solvent molecules becomes the same on both sides of the membrane, equilibrium is established. If the liquid outside is pure solvent, this condition can never be attained.

2. If the liquid rises in the tube to such a height that the resulting hydrostatic pressure increases the tendency of the solvent molecules inside the sac to leave it just enough to offset their smaller concentration, equilibrium is reached and osmosis ceases. The excess pressure, on the liquid inside the sac, which is just sufficient to prevent osmosis *when the liquid outside the sac is pure solvent*, is known as the *osmotic pressure* of the solution.

The pressure, exerted at equilibrium by the column of water in the tube (Fig. 5-7), is obviously not the osmotic pressure of the solution originally placed in the sac, because this original solution has been diluted by the solvent that flowed into the sac in attempting to establish equilibrium. In order to measure the osmotic pressure of the original solution, it is necessary to apply just enough external pressure on the liquid in the sac to prevent any change in its original volume.

Perfectly semipermeable membranes are difficult to obtain. The ones already mentioned are not perfectly semipermeable since they permit, to a greater or lesser extent, the passage of solute molecules. These membranes, if used in the apparatus in Fig. 5-7, cause only a temporary rise of liquid in the tube. After a while, the sugar molecules will diffuse slowly through the membrane until the concentrations inside and outside are the same. At this point, no osmotic pressure will be developed and the liquid levels inside and outside the sac will be the same.

One of the most satisfactory semipermeable membranes is prepared by putting a copper sulfate solution into a porous clay cup and setting the cup into a potassium ferrocyanide solution. Upon placing an anode inside the cup and a cathode outside, a gelatinous precipitate of copper ferrocyanide is deposited in the pores of the cup. This forms a membrane that not only is impermeable to many solutes, but also can withstand the high osmotic pressures developed by solutions.

van't Hoff's Theory of Solutions. In 1887 the Dutch chemist van't Hoff pointed out an interesting analogy between osmotic pressures and gas pressures. This analogy is summarized in van't Hoff's theory of solutions, as follows: The osmotic pressure of a dilute solution is the same as the gas pressure that would be developed by the solute if it were present as a gas, at the same temperature, in a volume equal to the volume of the solution.

It is found that osmotic pressures increase with rise in temperature, following the same rule (Charles's law) that gas pressures do. These relations are expressed in an equation similar in form to the ideal-gas equation.

$$\pi v = nRT \qquad (5\text{-}5)$$

In Eq. (5-5), π represents the osmotic pressure, n the number of moles of solute present, R the gas constant, and T the absolute temperature. The equation more nearly represents the actual behavior of solutions if v is the volume of the *solvent*, rather than that of the solution.

Equation (5-5) is an ideal equation and is followed approximately by actual solutions only when the concentration of the solute is small (0.1 molar or less). The behavior of any actual solution approaches that of the ideal as the solution becomes more and more dilute. Since osmotic pressure is proportional to concentration, it is possible, if we know the osmotic pressure of a solution, to calculate its concentration and from this its vapor pressure, boiling point, and freezing point.

Example 1. What is the osmotic pressure, at 20°C., of a solution containing 80.0 g. of sucrose (molecular weight = 342) in 500 ml. of solution?

$$\pi = \frac{nRT}{v} = \frac{\frac{80.0}{342} \text{ mole} \times 0.0821 \frac{\text{liter} \times \text{atm.}}{\text{mole} \times \text{°K.}} \times 293\text{°K.}}{0.500 \text{ liter}} = 11.3 \text{ atm.}$$

Example 2. How many grams of urea (molecular weight = 60) must be present in 800 ml. of solution to give an osmotic pressure of 15 atm. at 10°C.?

$$n = \frac{\pi v}{RT} = \frac{15 \text{ atm.} \times 0.800 \text{ liter}}{0.0821 \frac{\text{liter} \times \text{atm.}}{\text{mole} \times °K.} \times 283°K.} = 0.52 \text{ mole}$$

Weight of urea = 0.52 mole × 60 g./mole = 31 g.

If two or more solutes are present in the solution, each will behave as if it were present alone. The total osmotic pressure will be the sum of the individual osmotic pressures of the various solutes. When a membrane separates two solutions of different concentrations and is impermeable to the solute molecules of each solution, the pressure developed between the two solutions will be equal to the difference between the osmotic pressures of the individual solutions.

The above rules hold only for dilute solutions (0.1 molar or less). Physiological solutions are of this type. It is also assumed that the membrane is impermeable to all types of solute molecules. When this is not the case, a different condition arises, which will be discussed in the section on osmotic pressure in the living organism.

The analogy pointed out by van't Hoff, while useful, is in some respects misleading. It focuses attention on the solute and may give rise to the idea that osmotic pressure results directly from bombardment of the membrane by the solute molecules. The current belief is that this is incorrect. It is probable that the osmotic pressure is that exerted by the molecules of the solvent in their attempt to pass from a region of high solvent concentration to one of low solvent concentration. All that the solute does is to decrease the concentration of solvent on one side of the membrane.

Relation between Osmotic Pressure and Vapor Pressure. The osmotic pressure of a solution is a property of the solution and is independent of the nature of the membrane used to separate solution from solvent. To measure the osmotic pressure experimentally it is only necessary that the membrane be permeable to solvent molecules and impermeable to solute molecules. It would even be possible to have a membrane made of air. Such a case is illustrated in Fig. 5-8. In one of the beakers under the bell jar is an aqueous solution of a nonvolatile solute. In the

other beaker is pure water. These two liquids are separated by the air in the bell jar. This air is permeable to the solvent molecules in the form of vapor, but is impermeable to the nonvolatile solute molecules. The partial vapor pressure of the solvent in the solution is less than the vapor pressure of the pure solvent. Hence, solvent will distill from the beaker of pure solvent to the solution in an attempt to make their vapor pressures equal. This transfer of solvent answers the definition of osmosis.

If, by some means, the partial vapor pressure of the solvent in the beaker containing the solution could be made equal to the vapor pressure of pure water at the same temperature, there would be no transfer of solvent between the two beakers; *i.e.*, osmosis would not occur. We have seen, in Chap. 3, that it is possible to increase the vapor pressure of a liquid by increasing the external pressure on it. Hence,

Fig. 5-8. The relation between osmotic pressure and vapor pressure.

if a means could be devised for increasing the external pressure on the solution sufficiently, it would be possible to make the partial vapor pressure of the water in it equal to the vapor pressure of pure water. This would prevent osmosis. Note that the excess external pressure required to do this answers the definition of osmotic pressure. Thus we may redefine osmotic pressure as *the excess external pressure needed to make the partial vapor pressure of the solvent in the solution just equal to the vapor pressure of the pure solvent.* If, in Eq. (3-2), p_1 is the vapor pressure of the pure solvent and p_2 is the partial vapor pressure of the solvent in the solution, then $(P_1 - P_2)$ is the osmotic pressure of the solution.

Activity. In the preceding discussions of gases and solutions, it has repeatedly been stated that the laws, and expressions derived from them, are limited in their applicability. The ideal-gas equation holds only when the pressure—and therefore the concentration—of the gas is low. At high pressures, or concentrations, gases fail to follow this law. In a similar way it has
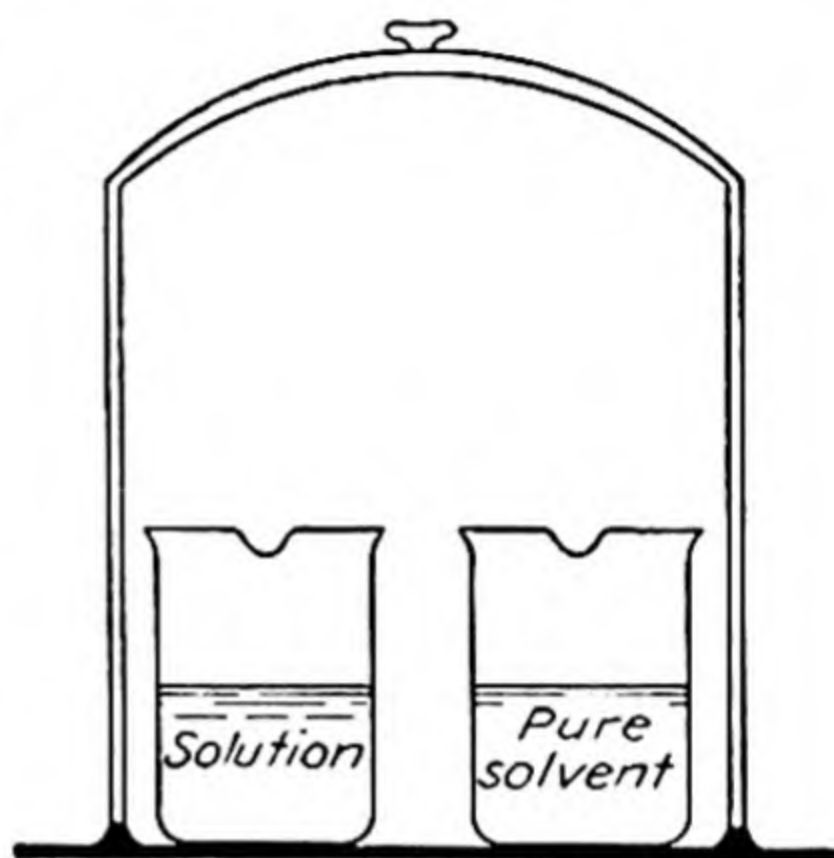
been found that the distribution law, Raoult's law, and the other laws governing the conduct of solutions, hold only for solutions in which the concentration of the solute is small. Solutions of higher concentrations fail to conform to these laws. The reasons for this lack of conformity in the case of gases have already been discussed. Somewhat similar reasons may be advanced to explain the failure of solutions to follow the laws. There may exist an intermolecular attraction between the molecules of a solute which prevents their independent action, thus making their concentration appear less than it actually is, or there may be a hydration of these solute molecules which decreases the amount of water capable of acting strictly as a solvent and thus produces the effect of an increased concentration of solute. In any case it is apparent that neither the pressure of a gas nor the osmotic pressure or vapor pressure of a solution can be taken as a true measure of the concentration of gas molecules or solute molecules, except for very low concentrations.

If, then, as indicated above, these properties do not measure concentration, what do they measure? G. N. Lewis answered this question by the statement that these properties are a measure, not of the concentration of the substance as ordinarily defined, but of its *effective concentration*, termed by him its *activity*. If the activity of a substance is substituted for its concentration in any of the expressions in which concentration appears, these expressions will then hold true regardless of the concentration of the substance. The usual symbol for activity is *a*.

For substances in the gaseous state, activities are expressed in terms of partial pressures. For solids and liquids, activities are expressed in terms of mole fractions. Thus, the activity of a pure solid or pure liquid is unity. The activity of a liquid acting as a solvent in a dilute solution approaches unity as its mole fraction approaches unity. For solutes, activities may be expressed in terms of mole fractions, molarities, or molalities. In the succeeding discussions in this book, it will be understood that when activities of solutes are used in connection with equilibriums in solution, they will be expressed in terms of molarities. On the other hand, when they are used in connection with electrode potentials, they will be expressed in terms of molalities. For dilute aqueous solutions, the difference between the values of the activity expressed in molarities and in molalities is so small that it is negligible.

The ratio between the activity of a substance and its concentration is known as the *activity coefficient* of the substance. The value of this activity coefficient will vary with the units in which the activity is expressed. When activities are expressed in terms of molarities the symbol used for the activity coefficient is f.

$$f = \frac{a}{M}$$

When activities are expressed in terms of molalities the symbol used for the activity coefficient is γ.

$$\gamma = \frac{a}{m}$$

For dilute aqueous solutions, the difference between the values of f and γ is negligible.

For both gases and solutions, as the concentration decreases, the molecules become more widely separated and are able to act more and more independently of each other. In other words, the effective concentration becomes more nearly equal to the actual concentration, or the activity coefficient approaches 1. It follows, therefore, that, in the dilute solutions with which we are principally concerned in physiological work, concentrations may be used without introducing any considerable error. For concentrated solutions, however, the equations will give accurate results only if activities are used.

Osmotic Pressure in the Living Organism. All living matter, whether plant or animal, is made up of cells. These cells may be pictured as composed of an elastic membrane enclosing an aqueous solution of various solutes. In many cases these cells are also surrounded by aqueous solutions. In plant cells the elastic membrane is enclosed by a more or less rigid sheath of cellulose, but in animal cells no such rigid protecting sheath exists. In both plant and animal cells the elastic membrane is semipermeable, permitting the passage of water molecules but preventing the passage of certain solute molecules and ions. The cellulose sheath that surrounds the membrane of plant cells is permeable both to solvent and solute molecules.

The existence of this semipermeable membrane in plant and animal cells suggests the possibility that osmosis may take place across it. It is found that this process actually occurs, water

flowing into or out of the cell, depending on whether the solute concentration inside is greater or less than that of the outside solution. Too great a flow of water in either direction impairs the functioning of the cell or may even destroy the cell. It is, therefore, important that equilibrium be maintained between the osmotic pressures of the internal and external solutions.

Osmosis in Plant Cells. Osmosis in plant cells may be observed by examining a thin film of onion skin under a microscope. In their normal condition, the cells are completely filled with liquid so that the membrane presses tightly against the outer sheath of cellulose, producing the condition of turgor found in the healthy plant (Fig. 5-9a). If the cell is brought in contact with a salt solution whose osmotic pressure is greater than that
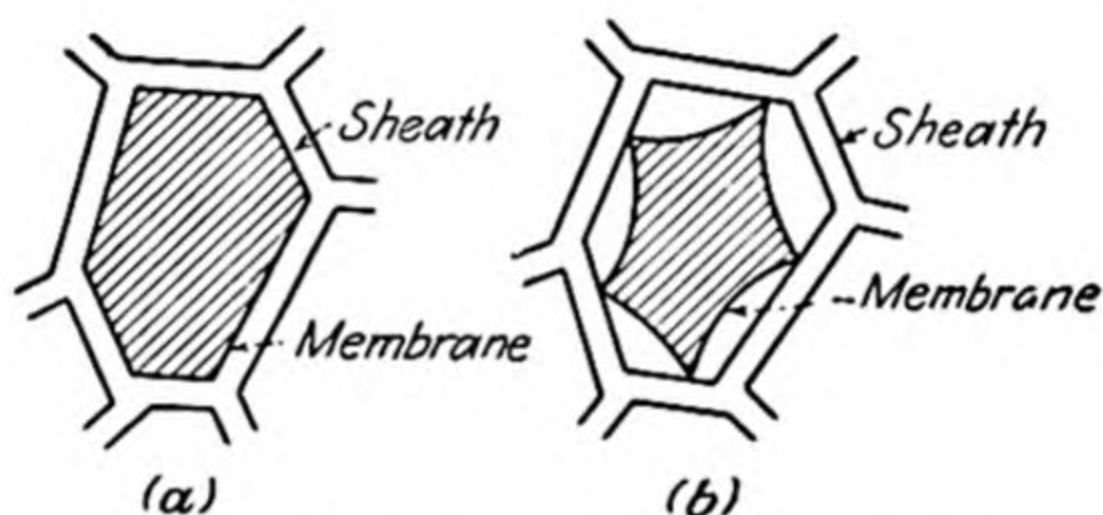
Fig. 5-9. Plasmolysis in a plant cell.

of the cell contents, osmosis takes place outward and the cell shrinks, pulling away from its outer sheath, as in Fig. 5-9b. Such a shrinking of the cell, caused by osmosis, is known as *plasmolysis*. The turgor of the cell may be restored by diluting the salt solution with water until its osmotic pressure is less than that of the cell contents. Osmosis then takes place inward, and the membrane is pressed tightly against the cellulose sheath, which keeps it from rupturing.

Osmosis in Animal Cells. The most important fluid in the body is the blood. It serves to carry oxygen and food to all parts of the body and to remove carbon dioxide and the other waste products. The osmotic-pressure relations in the blood, therefore, may well be chosen as an example of osmosis in animal cells.

Composition of Blood. Blood may be considered as made up of two main components: (1) the fluid medium which is known as the plasma, and (2) the various types of cells, such as the red

and white corpuscles, that are suspended in the plasma. In Table 5-2 is listed the approximate composition of human blood plasma. The percentages of the different components may vary widely in different persons.

TABLE 5-2. APPROXIMATE COMPOSITION OF HUMAN BLOOD PLASMA

Component	Per Cent
Proteins:	
Albumin	4.5
Globulin	2.2
Fibrinogen	0.3
Prothrombin, etc	0.5
Other organic substances	0.5
Inorganic salts	1.0
Water	91.0

Fibrinogen is the substance responsible for the clotting of blood. If blood, or blood plasma, is to be kept for any length of time for experimental work, it is desirable to prevent clotting. Clotting may be prevented by the removal of calcium ions from the blood by the addition of oxalate or citrate ions. It may also be prevented by removing fibrinogen. This removal may be accomplished by stirring the blood briskly, or by shaking it with glass beads. As the fibrinogen turns to fibrin, the latter clings in strings to the rod, or to the beads, and may be removed. The liquid remaining after fibrinogen has been removed from blood plasma is known as *blood serum*. Many of the properties of serum are practically the same as those of plasma. Since the serum does not clot, it is useful for experimental work.

Of the various cells suspended in the plasma, the red corpuscles may be selected for consideration. These cells consist of a semipermeable membrane enclosing a liquid whose approximate composition is given in Table 5-3. There may be considerable variation from the percentages listed in that table.

Hemoglobin is the oxygen carrier in the blood and is also the material that confers the red color to blood. The corpuscles may be separated from the plasma by centrifuging.

TABLE 5-3. APPROXIMATE COMPOSITION OF RED CORPUSCLES

Component	Per Cent
Hemoglobin	32
Other organic substances	7
Inorganic salts	1
Water	60

Osmotic Pressure of the Blood Serum. The osmotic pressure of the blood serum depends principally on the concentration of the salts dissolved in it. The proteins and the corpuscles present have such a high molecular weight that the amounts present give a molar concentration so low that their effect on the osmotic pressure is very slight. Of an osmotic pressure of the blood equal to 580 cm. of Hg, it is estimated that the proteins are responsible for only 3 to 4 cm. of Hg, or less than 1 per cent.

Slight, however, as this protein osmotic pressure is, it is believed to be the controlling factor in maintaining the proper water balance between the blood and the tissues. According to Clark,[1] "There are good reasons for believing that *some* blood capillaries are permeable to all the principal constituents of plasma other than proteins." If this is the case, then, as we shall see in the discussion of *tone*, the movement of water into, or out of, the capillaries will be controlled by the concentration of the proteins in the plasma. If for any reason the concentration of plasma proteins is decreased, as it may be by starvation, by damage to the kidneys, or by pathological changes in the permeability of the capillary walls, the osmotic pressure of the plasma is decreased and consequently there should be a flow of water from the plasma to the interstitial fluid in the tissues outside the capillaries. The resulting puffiness of the tissues is called *edema*.

This osmosis may be overcome temporarily by the injection of saline solutions. However, since the capillary walls are permeable to the ions in the saline solution, the relief is only temporary. Longer lasting relief is obtained by the intravenous injection of concentrated blood plasma, which contains a higher concentration of proteins than does normal blood plasma. This raises the osmotic pressure of the blood and tends to draw back into the blood stream the water originally lost.

One of the several factors involved in shock is the diminution of the blood volume and, according to Clark, it is on the principle discussed above "that the practical, immediate and often critically important treatment of shock depends in large measure."

The osmotic pressure of the blood serum is usually measured indirectly by determining its freezing point. The average freezing point of human blood serum is −0.56°C. Since a 1 molal

[1] CLARK, W. M., "Topics in Physical Chemistry," p. 113, The Williams & Wilkins Company, Baltimore, 1948.

solution freezes at $-1.86°C.$, the effective molality of the serum equals $0.56/1.86 = 0.30$ molal. From this value the osmotic pressure of the serum at the temperature of blood ($38°C.$) may be calculated.

$$\pi = \frac{0.30 \text{ mole} \times 0.0821 \dfrac{\text{liter} \times \text{atm.}}{\text{mole} \times °\text{K.}} \times 311°\text{K.}}{1.00 \text{ liter}} = 7.7 \text{ atm.}$$

This value is held almost constant by the elimination of excess salts in the urine. If, because of impairment of the kidneys, the excess salts in the blood are not eliminated, the freezing point of the serum may drop as low as $-1.04°C.$

Osmotic Pressure of the Contents of the Red Corpuscle. The osmotic pressure of the solution inside the red corpuscle cannot be measured directly because this would involve the destruction of the cell. It is necessary, therefore, to determine this osmotic pressure by comparing the cell with a solution whose osmotic pressure is known. Before discussing the method by which this is done, it is necessary to introduce and discuss a new term, the *tone* of a solution, and to differentiate between tone and osmotic pressure.

It has already been stated that if two solutions have the same molar concentration they will have the same osmotic pressure, or will be isosmotic, and no osmosis will take place between them. The last phrase of that statement is true only if the two solutions are separated by a perfectly semipermeable membrane, *i.e.*, one that is permeable only to solvent molecules and entirely impermeable to all solute molecules. Membranes of this type are uncommon. The varieties commonly used in osmotic-pressure work, such as the membrane surrounding the red corpuscle, are imperfectly semipermeable, being permeable not only to solvent molecules but to some types of solute molecules as well.

When such a membrane separates the two solutions, the motion of fluid across the membrane is controlled, not by the total concentration of solute molecules in each solution, but rather by the concentration of those molecules which cannot pass through the membrane. This concentration of solute molecules that cannot cross the membrane used determines the tone of the

solutions. The distinction between osmotic pressure and tone may be illustrated by the following series of examples.[1]

Assume a membrane that is permeable to water and to urea but is impermeable to sugar and to glycerin. This membrane is used to separate various solutions as indicated in Fig. 5-10. In (a), the solutions inside and outside the membrane have the same concentration, so they are isosmotic. The membrane is impermeable to both kinds of solute molecules. There will be no transfer of solvent molecules and no change in the volume of the contents of the membrane sac. In this case the two solutions are said to have the same tone, or to be *isotonic*. In (b), the two solutions, being of the same molar concentration, are isosmotic. But the membrane is permeable to urea as well as to
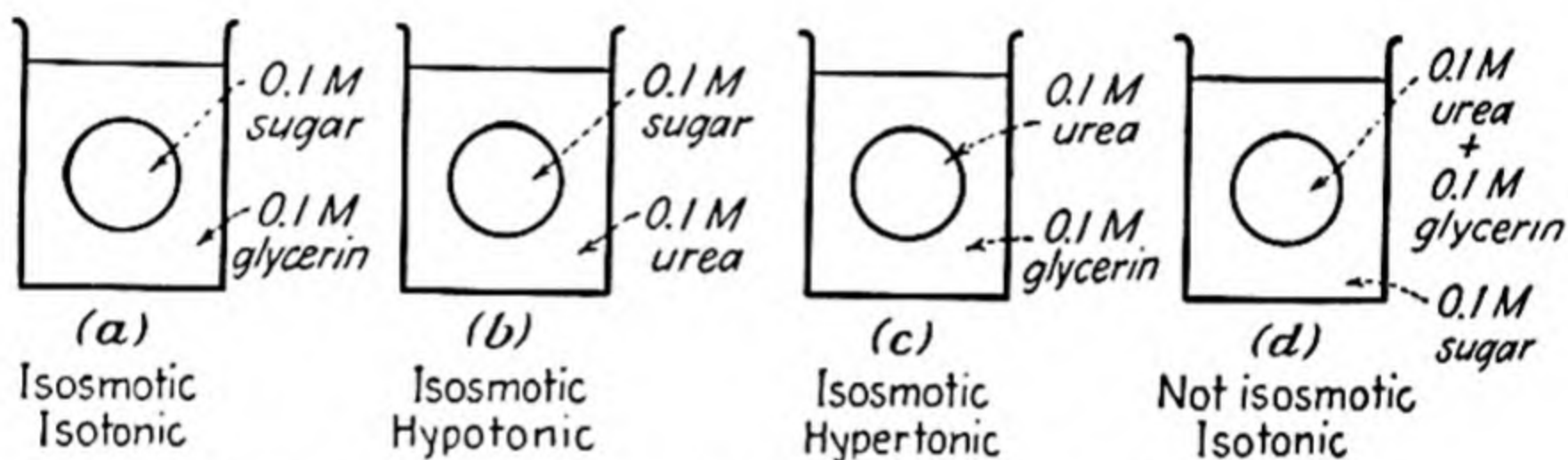
FIG. 5-10. Difference between tone and osmotic pressure.

water, so this system behaves as if there were pure water on the outside of the sac, instead of water and urea. In other words, the membrane is unable to distinguish between water and urea and behaves toward the mixture as if it were water. In this case, therefore, liquid will pass from the outside to the inside of the sac, increasing the volume inside and swelling the sac. The outside solution is said to have a lower tone than the inside solution, or is *hypotonic* with respect to it.

This transfer of liquid may be pictured as taking place in the following steps: (1) Urea will pass from the outside to the inside until equilibrium has been established between the urea molecules in the two solutions. (2) The preceding change decreases the concentration of water inside and increases the concentration of water outside; therefore, water will pass from

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[1] For simplicity, we shall assume that there is no ionization. If the nondiffusible particle is an ion, the situation is changed. See the section on the Donnan equilibrium in Chap. 12.

outside to inside to restore equilibrium. This results in an increase in the volume of the contents of the sac.

Following the same line of reasoning, it is apparent that in case (c) the conditions are reversed and liquid will move out of the sac, allowing it to shrink. This action is similar to plasmolysis in plant cells, although in this case, as in animal cells, there is no protecting sheath of cellulose around the cell membrane. In this case the two solutions are isosmotic, but the outside solution has a higher tone than the inside one, or is *hypertonic* with respect to it.

In case (d), the inside solution is twice as concentrated as the outside one, so that the two solutions are not isosmotic. It should be noted, however, that the membrane is permeable to urea. In this case the movement of urea molecules out of the sac is balanced by the movement of water molecules into the sac, so that at equilibrium no net change in volume has taken place. Essentially, this system behaves as if there were nothing but water and glycerin inside the sac; the sac will neither swell nor shrink. The two solutions, therefore, are isotonic.

This behavior of solutions may be summarized as follows: The osmotic pressure of a solution is determined by the total concentration of solute molecules; the tone of a solution is determined by the concentration of those solute molecules which cannot pass the membrane used.

The osmotic pressure of a solution is a colligative property of that solution. It is related to the freezing-point depression of the solution and is independent of the nature of the membrane which may surround the solution. The tone of a solution is not necessarily a colligative property of the solution. It is not necessarily related to the freezing-point depression of the solution and is dependent upon the permeability, to the solute molecules, of the membrane which surrounds the solution.

Returning to the consideration of the red corpuscles, since the membrane that encloses them is permeable to certain solutes, it is possible to determine the tone of the contents, but not their osmotic pressure. This determination of tone may be accomplished by placing the corpuscles in contact with a solution of salt, since the cell membrane is impermeable to sodium chloride. If this is done with varying concentrations of sodium chloride, it is found that in some cases the cell will swell, indicating that the

salt solution is hypotonic, and in other cases the cell will shrink, indicating that the salt solution is hypertonic. An approximately 0.9 per cent solution of sodium chloride will produce no volume change in the cell, showing that this solution is isotonic with the cell contents. That is, the osmotic pressure of a 0.9 per cent solution of sodium chloride is the same as the osmotic pressure of that portion of the cell contents which cannot pass the cell membrane. This value for the tone of the red cells is to be expected in view of the fact that the osmotic pressure of the blood serum has been found to be equal to that of a 0.9 per cent sodium chloride solution, and the red corpuscles do not undergo volume changes in the serum.

If a more dilute solution of sodium chloride is used, it is hypotonic with respect to the cell contents, and the resultant flow of water into the cell will increase its volume. The cell membrane is elastic and can stand a certain amount of swelling, but if the concentration of salt is reduced to approximately 0.47 per cent, the inflow of liquid stretches the membrane to the point where it allows some of the hemoglobin to leak through, staining the surrounding solution red. Such a passage of hemoglobin through the membrane is known as *hemolysis*. The concentration of salt required to produce hemolysis is a measure of the strength of the cell membrane and has some value in diagnosis.

Any fluid to be injected into the blood stream should be isotonic with the cell contents. This is insured by dissolving the material to be injected in a salt solution so made up that it has approximately the same tone as do the contents of the cell. Such a solution is known as a *physiological salt solution*. For reasons that will be discussed in the next chapter, it is necessary that a physiological salt solution should not only be isotonic with the cell contents, but should also contain definite concentrations of specific solutes. Of the solutions that meet these requirements, a commonly used one is Locke's solution.

TABLE 5-4. COMPOSITION OF LOCKE'S PHYSIOLOGICAL SALT SOLUTION

Component	Grams per 100 ml. of Solution
Sodium chloride	0.9
Potassium chloride	0.042
Calcium chloride	0.024
Sodium bicarbonate	0.02
Glucose	0.1

Permeability of the Cell Membrane. It is possible to determine in the following way what substances will or will not pass the cell membrane. Make up a series of solutions that contain 0.9 per cent sodium chloride and, in addition, some one of the substances to be tested. In each solution, place some red corpuscles. The 0.9 per cent sodium chloride is isotonic with the cell contents and so produces no change in the cell volume. If the substance added permeates the cell membrane, it does not change the tone of the salt solution and does not produce any permanent change in the volume of the cell.[1] On the other hand, if the added substance does not permeate the cell membrane, it increases the tone of the salt solution and the red corpuscle shrinks. Much of the experimental work on the permeability of red corpuscles has been done on blood other than human blood.[2] The work done on human red corpuscles indicates that the membrane surrounding them is permeable to monosaccharides and to hydronium, hydroxide, chloride, and bicarbonate ions. It is permeable to a smaller degree to glycerin and is practically impermeable to disaccharides, amino acids, the higher polyhydric alcohols, and sodium and potassium ions.

Problems

1. A 15 weight per cent solution of a nonvolatile solute in water has a vapor pressure, at 20°C., equal to 16.8 mm. of Hg. What is the molecular weight of the solute?

2. What is the vapor pressure, at 20°C., of a 20 weight per cent solution of sucrose in water? The molecular weight of sucrose is 342.

3. A solution containing 10 g. of solute in 200 g. of water freezes at −0.6°C. What is the molecular weight of the solute?

4. What is the boiling point of a solution containing 10 g. of urea in 100 g. of water? The molecular weight of urea is 60.

5. What is the molality of a solution in benzene that freezes at +2.0°C.?

6. What is the boiling point of a solution containing 10 g. of sucrose in 100 g. of ethyl alcohol?

7. Calculate the freezing point and the boiling point of a water solution whose vapor pressure, at 20°C., equals 17.0 mm. of Hg.

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[1] A temporary volume change may be produced owing to the difference in the speeds with which water and the added substance diffuse across the membrane. By the time equilibrium has been reached, however, the cell will have returned to its original volume.

[2] For a discussion of the subject, see H. Davson, and J. F. Danielli, "The Permeability of Natural Membranes," The Macmillan Company, New York, 1943.

8. Calculate the osmotic pressure, at 18°C., of a 10 weight per cent solution of sucrose in water.

9. A solution containing 7 g. of solute in 150 ml. of water has an osmotic pressure, at 10°C., of 10 atm. What is the molecular weight of the solute?

10. What is the osmotic pressure, at 15°C., of a solution containing 30 g. of sucrose and 30 g. of urea in 1 liter of water?

11. Calculate the pressure, at 20°C., between a solution containing 30 g. of sucrose in 500 ml. of water and a solution containing 30 g. of urea in 1 liter of water.

12. A water solution of a nonvolatile solute has an osmotic pressure, at 20°C., equal to 15 atm. What is the vapor pressure of this solution, at 20°C., and what is its freezing point?

13. Given stock solutions of sodium chloride, potassium chloride, calcium chloride, sodium bicarbonate, and glucose, each of which is 0.5 molar, show how you should proceed to make up 1 liter of Locke's solution.

14. In each of the following cases, tell whether the solutions are isosmotic or not. Also tell whether the external solution is isotonic, hypertonic, or hypotonic with respect to the internal solution. The membrane used is permeable to water and to urea but is impermeable to sugar and to glycerin.

Solution	A	B	C
Internal..............	0.1M urea 0.1M sugar	0.1M glycerin	0.2M sugar
External..............	0.2M glycerin	0.1M urea 0.1M sugar	0.1M urea 0.1M glycerin

15. Toluene and water are immiscible. In the following table are given the vapor pressures of each of these liquids at various temperatures.

Toluene, $C_6H_5CH_3$ Density = 0.87 g./cm.³		Water, H_2O Density = 1.0 g./cm.³	
Temperature, °C.	Vapor pressure, mm. of Hg	Temperature, °C.	Vapor pressure, mm. of Hg
60	140	60	149
70	202	65	187
80	290	70	234
90	405	75	289
100	557	80	355
110	760	85	433
		90	526
		95	634
		100	760

Plot the above data, and determine the approximate temperature at which a mixture of toluene and water will boil. Calculate the proportions by weight, and by volume, of toluene and of water in the distillate.

16. For the solution of A and B shown in Fig. 5-3 calculate the vapor pressure of the solution containing 30 mole per cent of B. Also calculate the mole per cent of B in the vapor which is in equilibrium with this solution.

17. Using Eq. (3-2) calculate the osmotic pressure of an aqueous solution whose vapor pressure is 12.0 mm. of Hg, if the vapor pressure of pure water, at the same temperature, is 12.7 mm. of Hg. Temperature = 15°C.

CHAPTER 6

PROPERTIES OF SOLUTIONS OF ELECTROLYTES

When the colligative properties of solutions that conduct electricity are studied, it is found that these solutions do not show the same uniformity of behavior shown by solutions of nonelectrolytes. In each case the electrolyte solution exhibits distinct abnormalities. If the solute is nonvolatile the vapor-pressure lowering and the boiling-point elevation are greater than expected; also the freezing-point depression and the osmotic pressure are more than the normal amount. The extent of these abnormalities for some aqueous solutions is indicated in Table 6-1. In this table are given the data for a nonelectrolyte, sugar, and for two electrolytes, potassium chloride and barium chloride. These data show the osmotic pressures of solutions of these substances at two different concentrations. The first line under each concentration gives the value that the solution should show if the solute behaved normally. The second line gives the experimentally determined value. It is to be noted that for the two electrolytes the observed value is in excess of the normal value. If any of the other colligative properties of these solutions had been measured, similar abnormalities in their values would have been observed.

The van't Hoff Factor. The value of i, given in the third line of each group in Table 6-1, expresses the degree of abnormality of the solution. This degree of abnormality is the ratio between the observed and the normal values of any of the colligative properties of the solution.

$$i = \frac{\text{observed value of colligative property}}{\text{normal value of colligative property}} \tag{6-1}$$

The expression i is known as the *van't Hoff factor* of the solution. For nonelectrolytes the value of i is unity at all concentrations.[1] For electrolytes, however, the value of i is greater than 1.0, being

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[1] See, however, the section on activity in Chap. 5.

TABLE 6-1. ABNORMALITY OF SOLUTIONS OF ELECTROLYTES

	Solute		
	Sugar, $C_{12}H_{22}O_{11}$	Potassium chloride, KCl	Barium chloride, $BaCl_2$
Concentration = 0.01 molar Normal osmotic pressure, at 0°C..................	0.224 atm.	0.224 atm.	0.224 atm.
Observed osmotic pressure, at 0°C..................	0.224 atm.	0.435 atm.	0.610 atm.
Value of i.................	1.0	1.94	2.72
Concentration = 0.001 molar Normal osmotic pressure, at 0°C..................	0.0224 atm.	0.0224 atm.	0.0224 atm.
Observed osmotic pressure, at ˙0°C..................	0.0224 atm.	0.0442 atm.	0.0648 atm.
Value of i.................	1.0	1.97	2.85
Maximum value of i at infinite dilution..................	1.0	2.0	3.0

more for some types of electrolytes, such as barium chloride, than it is for others, such as potassium chloride. Furthermore, for these electrolytes the value of i increases as the solution becomes more dilute, until at infinite dilution it approaches a maximum. The maximum value of i for potassium chloride is 2.0, while for barium chloride it is 3.0.

Example. A solution containing 4 g. of sodium hydroxide in 200 g. of water freezes at −1.7°C. Calculate the value of the van't Hoff factor for this solution. The solution contains 20 g. of sodium hydroxide in 1,000 g. of water. Therefore it is a 0.50 molal solution, and its normal freezing point should be −0.93°C.

$$i = \frac{\text{observed freezing-point depression}}{\text{normal freezing-point depression}} = \frac{1.7°C.}{0.93°C.} = 1.8$$

From this value of i the values of the other colligative properties of the solution may be calculated. The value of i usually increases as the temperature rises. Therefore values of the other colligative properties, calculated from the value of i, will be valid only for the temperature at which i was determined.

Example. What is the osmotic pressure, at 0°C., of the solution described in the preceding example? Assume that the value of i is the same at 0°C. as it is at −1.7°C. The normal osmotic pressure of a 0.50 molal solution at 0°C. is 11.2 atm. Since the degree of abnormality of this solution is 1.8, its osmotic pressure, at 0°C., should be $1.8 \times 11.2 = 20$ atm.

Theory of Electrolytic Dissociation. It was shown in Chap. 5 that the colligative properties of solutions of nonvolatile non-electrolytes were related to the molality of the solution and were independent of the chemical nature of the solute. Since solutions of the same molality contain the same number of solute molecules per 1,000 g. of solvent, it appears that the colligative properties are determined by the number of solute particles (in this case, molecules) present and not by their chemical nature. Therefore, all molal aqueous solutions should give the same value for the freezing-point depression and the other colligative properties. There exists, however, a large class of solutes, the electrolytes, to which this rule obviously does not apply. A water solution of any member of this class behaves as if it contained more solute molecules[1] than it actually does. The most reasonable explanation of this discrepancy that has been advanced is that the molecules of electrolytes, in water solution, are capable of breaking down, or dissociating, into smaller particles, each of which has the same effect on the colligative properties of the solution as does a whole molecule. Further evidence as to the nature of these particles is gained from the fact that solutions of electrolytes conduct electricity. This indicates that the particles into which the molecule is dissociated bear an electrical charge and so are attracted to electrodes inserted into the solution.

This explanation of the behavior of electrolytes in solution is summarized in Arrhenius' theory of electrolytic dissociation, or ionization theory. The main points of this theory are as follows:

1. Molecules of electrolytes in water solution are dissociated into two or more particles called *ions*. An ion may be composed

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[1] While it is true, as we shall see, that there is no such thing as a molecule of sodium chloride, or other electrovalent compound, in the solid state or in solution, nevertheless it will be convenient to use the terms *molecule* and *molecular weight* in referring to these substances. By molecule we shall mean the combination of atoms represented by the formula usually written for the substance; by molecular weight we shall mean the sum of the atomic weights of the atoms in that formula.

of a single atom, such as the cupric ion, Cu^{++}, or may be a group of atoms which acts as a unit, such as the sulfate ion, SO_4^{--}.

2. Each ion has the same effect on the colligative properties of the solution as does a whole molecule.

3. Each ion bears an electrical charge, either positive or negative, and it is the motion of these charged particles through the solution that carries the electrical current. The positive ions are called *cations*, and the negative ions are called *anions*.

The motion of ions can be demonstrated by the following experiment. A brown solution of cupric dichromate is prepared by mixing equal volumes of molar solutions of cupric sulfate and potassium dichromate. To this is added a few drops of dilute
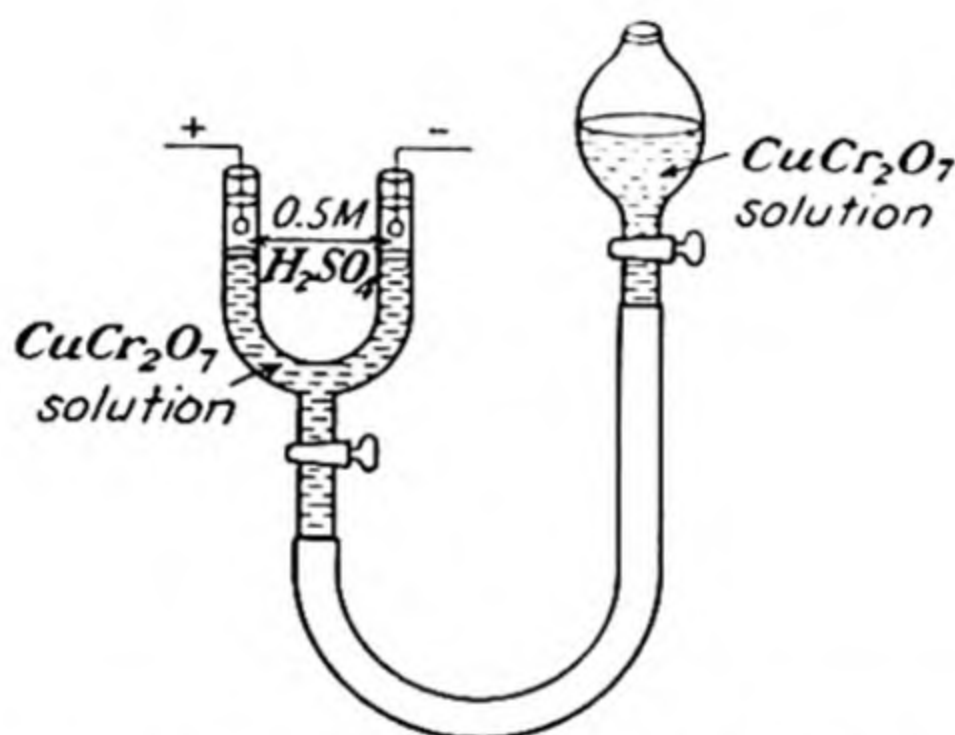
FIG. 6-1. Apparatus for demonstrating the motion of ions.

sulfuric acid to prevent hydrolysis. This solution is placed in the apparatus shown in Fig. 6-1 so that the leveling bulb and all the tube between the two stopcocks is filled with the solution and free from air bubbles. The U tube above its stopcock should be rinsed out and enough 0.5M sulfuric acid added to fill the curved part of the tube. Now allow the cupric dichromate solution to flow very slowly into the U tube until the liquid level is raised nearly to the top of both arms of the tube. If this is done carefully there will be a sharp boundary between the colorless sulfuric acid and the brown dichromate solution. Insert inert electrodes into the sulfuric acid in each arm, and connect them to a source of direct current. A storage battery furnishing 20 volts is satisfactory, or a 110-volt or 220-volt direct-current lighting circuit can be used if a lamp is placed in series with it to limit the current

to about 0.25 amp. In about 10 minutes the blue of the cupric ions will be visible at the boundary nearest the cathode, while the orange color of dichromate ions will appear at the boundary nearest the anode.

The electrode at which electrons *enter* the solution is known as the *cathode*. The positively charged cations migrate toward the cathode. The electrode at which electrons *leave* the solution is known as the *anode*. Toward this electrode the negatively charged anions migrate.

Determination of the Charge on an Ion. By means of experiments similar to that illustrated in Fig. 6-1, it is possible to determine the nature of the charge, positive or negative, on the ions of any electrolyte. The amount of this charge remains to be determined; *i.e.*, whether or not all cations carry the same amount of positive charge, and whether all anions carry the same amount of negative charge. This problem may be solved in the following way. If an electric current is passed through a solution of nickel chloride, the nickel ions migrate to the *cathode* and, upon reaching it, take electrons from it. These electrons neutralize the positive charge on the nickel ions, and metallic nickel then deposits on the electrode. At the same time, chloride ions are moving to the *anode*, and upon reaching it release their excess electrons to it and become neutral gaseous chlorine. This decomposition of a solute by electricity is known as *electrolysis*.

If the electrolysis of nickel chloride is continued long enough, 1 mole of nickel ion will be neutralized at the cathode, and at the same time, 2 moles of chloride ion will be released at the anode.[1] This process results in the transfer of 2 faradays of electricity across the solution. That is, 1 mole of nickel ion picks up 2 faradays of electrons from the cathode, and at the same time, 2 moles of chloride ion release 2 faradays of electrons to the anode. Thus it appears that 1 mole of nickel ion carries 2

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[1] The term "mole," when referring to ions, means the mass, in grams, equal to the sum of the atomic weights of all the atoms appearing in the formula of the ion in question. For example, a mole of nickel ion, Ni^{++}, is 58.69 g.; of ammonium ion, NH_4^+, is 18 g.; and of sulfate ion, SO_4^{--}, is 96 g. A mole of an ion is not necessarily equal to a mole of the element from which the ion is derived. For example, a mole of chlorine gas, Cl_2, is 70.92 g., but a mole of chloride ion, Cl^-, is only 35.46 g. The important characteristic of the mole, referring to ions, is that a mole of any ion contains the same number (6.02×10^{23}) of individual ions as does a mole of any other ion.

faradays, while 1 mole of chloride ion carries only half that amount, or 1 faraday.

If the ions of all electrolytes are examined in this way, it is found that the smallest quantity of electricity associated with 1 mole of any ion is 1 faraday. If 1 mole of any ion carries a greater amount of electricity, such amount is always an integral multiple of 1 faraday. In explanation of these facts it is assumed that each faraday carried by a mole of an ion represents a unit charge on that ion. Thus, in the examples already cited, 1 mole of nickel ion carries 2 faradays and is written Ni^{++}, while 1 mole of chloride ion carries 1 faraday and is written Cl^-. Some of the more commonly occurring ions, with their charges, are listed in Table 6-2.

TABLE 6-2. IONIC CHARGES

Cations	Anions
Hydronium, H_3O^+	Hydroxide, OH^-
Sodium, Na^+	Chloride, Cl^-
Potassium, K^+	Nitrate, NO_3^-
Ammonium, NH_4^+	Sulfate, SO_4^{--}
Magnesium, Mg^{++}	Phosphate, PO_4^{---}
Calcium, Ca^{++}	Carbonate, CO_3^{--}
Barium, Ba^{++}	Acetate, $C_2H_3O_2^-$
Silver, Ag^+	
Ferrous, Fe^{++}	
Ferric, Fe^{+++}	
Aluminum, Al^{+++}	

Gram-equivalent. It has already been stated that 1 mole of an ion contains the same number of individual ions as does 1 mole of any other ion. It will, at times, be very convenient to have another unit of quantity, so defined that this quantity of any ion will carry the same number of positive charges, or of negative charges, as does a like quantity of any other ion. The unit that satisfies these requirements is known as the *gram-equivalent*, or *equivalent weight*, of the ion. The significance of this term will be apparent from a consideration of Table 6-3.

The second column in the left half of Table 6-3 gives the mass of 1 mole of the ion. This quantity contains the same number (6.02×10^{23}) of individual ions in each case. It will be noted, however, that 1 mole of calcium ion carries twice as many positive charges as does 1 mole of sodium ion. Therefore, to obtain an

amount of calcium ion carrying the same number of positive charges as does 1 mole of sodium ion, it is necessary to divide the mole of calcium ion by two, which is the number of charges appearing on a single ion. This number of charges also represents the valence of the ion. The quantities so obtained for each ion appear in the third column of the table and are known as the gram-equivalents of the ions. Each of these gram-equivalents carries the same number (6.02×10^{23}) of positive or of negative charges. In the electrolysis of solutions, the passage of 1 faraday of electricity results in the simultaneous release of 1 gram-equivalent of cation at the cathode and 1 gram-equivalent of anion at the anode.

This idea of equivalent weights can be extended to solutes. The equivalent weight of a solute, with respect to one of its ions,

TABLE 6-3. RELATION BETWEEN THE MOLE AND THE GRAM-EQUIVALENT

Ion	1 mole	1 gram-equivalent	Molecule	1 mole	1 gram-equivalent
H_3O^+	19.02 g.	19.02 g.	HCl	36.47 g.	36.47 g.
Na^+	23.00	23.00	Na_2SO_4	142.06	71.03
Ca^{++}	40.08	20.04	$AlCl_3$	133.35	44.45
Al^{+++}	26.97	8.99	$Al_2(SO_4)_3$	342.12	57.02
OH^-	17.01	17.01			
Cl^-	35.46	35.46			
SO_4^{--}	96.06	48.03			
PO_4^{---}	94.98	31.66			

is equal to the molecular weight of the solute divided by the total number of charges on the ions, of the species referred to, obtained from the dissociation of one molecule of solute. When the solute furnishes only two kinds of ions, as is the case for those solutes listed in the right half of Table 6-3, the equivalent weight is the same with respect to either ion. Each of these equivalent weights, if completely dissociated, will furnish the same total number of charges, i.e., 6.02×10^{23} positive charges and 6.02×10^{23} negative charges.

If, however, the solute furnishes more than two kinds of ions, the equivalent weight may vary with the ion to which it is referred. It is then necessary to specify the ion when giving the equivalent

weight of the solute.   In the case of disodium ammonium phosphate, which dissociates as follows, $Na_2NH_4PO_4 \rightarrow 2Na^+ + NH_4^+ + PO_4^{---}$, the equivalent weight with respect to the ammonium ion is the same as the molecular weight, but with respect to the sodium ion is one-half the molecular weight, and with respect to the phosphate ion is one-third the molecular weight.

The above definitions and examples of equivalent weights are valid for substances taking part in double decompositions.   It is possible, however, for some of these substances to serve as oxidizing or reducing agents.   In such a case the equivalent weight has a different definition and may have a different value.   The equivalent weight of an oxidizing or reducing agent, either ion or molecule, is its molecular weight divided by the number of electrons gained or lost by the ion or molecule in the oxidation-reduction reaction.   For example, in double decompositions the equivalent weight of ferrous sulfate, $FeSO_4$, is one-half its molecular weight, but in oxidation-reduction reactions, in which it loses one electron per molecule, its equivalent weight is the same as its molecular weight.

Normal Solutions.   In the discussion of solutions in Chap. 4, it was shown that molar solutions are so made up that equal volumes of solutions of the same molarity contain the same number of solute molecules.   Normal solutions, on the other hand, are so prepared that equal volumes of solutions of the same normality, for double decompositions, contain the same number of positive or negative charges, if the solute is completely dissociated.   These normal solutions can be prepared by dissolving 1 gram-equivalent of solute in enough water to make 1 liter of solution.   The usual symbol for normality is N.   Thus the expression $0.3N$ H_2SO_4 refers to a solution containing 0.3 gram-equivalent of sulfuric acid in each liter of solution.

If the solute furnishes more than two kinds of ions it is necessary to specify tho ion with respect to which the normality of the solution is given.   It should also be noted that if the solution is to serve as an oxidizing or reducing agent its normality may differ from that when it takes part in double decompositions.

The advantage of expressing concentrations in terms of normalities is found in the calculations of volumetric quantitative

analysis. For example, equal volumes of all acids and bases of the same normality are capable of furnishing the same number of hydronium ions and hydroxide ions and so are equivalent to each other according to the reaction

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

Similarly, the number of silver ions in 10 ml. of $1.0N$ silver nitrate is the same as the number of chloride ions in 10 ml. of a normal solution of sodium chloride, or of barium chloride, or of ferric chloride. Therefore, if the silver nitrate solution is added to an equal volume of any of the other solutions, the silver ions and chloride ions are quantitatively precipitated as silver chloride according to the reaction

$$Ag^+ + Cl^- \rightarrow AgCl$$
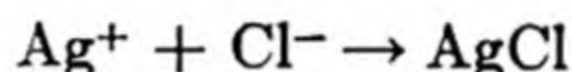
The extent to which the normality of a solution is changed by dilution may be calculated by an equation similar to that used for determining changes in molarity.

$$\text{Volume} \times \text{normality} = \text{volume} \times \text{normality} \qquad (6\text{-}2)$$
$$\text{(Before dilution)} \qquad\qquad \text{(After dilution)}$$

A similar equation may be used in problems involving the titration of an acid against a base. Equal numbers of hydronium ions and hydroxide ions neutralize each other; therefore, the number of hydronium ions originally present in the acid must equal the number of hydroxide ions present in the amount of base added to reach the equivalence point. From this it follows that, at the equivalence point of the titration,

$$\text{Volume} \times \text{normality} = \text{volume} \times \text{normality} \qquad (6\text{-}3)$$
$$\text{(Acid)} \qquad\qquad \text{(Base)}$$

Example. If 17 ml. of $2.3N$ sodium hydroxide is neutralized by 28 ml. of sulfuric acid, what is the normality and molarity of the acid?

$$17 \times 2.3 = 28 \times x$$
$$x = \frac{17 \times 2.3}{28} = 1.4 \text{ normal}$$
$$\text{Molarity} = \frac{1.4}{2} = 0.70 \text{ molar}$$

A similar useful relationship exists between the normalities of solutions that act as oxidizing and reducing agents.

$$\text{Volume} \times \text{normality} = \text{volume} \times \text{normality} \qquad (6\text{-}4)$$
$$\text{(Oxidizing solution)} \qquad \text{(Reducing solution)}$$

ELECTROVALENT AND COVALENT BONDS

Before going on to examine the means of measuring the extent to which dissociation takes place, it will be well to consider the forces holding atoms together in compounds and to see why some substances are electrolytes while others are not.

Determination of the structure of atoms indicates that the inert gases, with the exception of helium, all have eight electrons in their outermost orbit.[1] Since these gases are chemically inactive, it is believed that this number, eight electrons, represents a very stable arrangement. Elements not possessing this stable arrangement will strive to reach it in reaction with other elements by gaining, losing, or sharing electrons, thus forming chemical compounds. The number of electrons gained, lost, or shared determines the valence of the element in the compound. The ease with which they are gained, lost, or shared determines the energy of the reaction.

Two main types of valence bonds result from these reactions, depending on whether electrons are actually transferred from one reactant to the other or are shared between the two.

Electrovalence. We may picture the neutral sodium atom as Na·, where the symbol Na represents the *kernel* of the atom, *i.e.*, the nucleus and all electrons except those in the outermost orbit, and the dot represents the single electron in the outermost orbit. In the same way, we may picture the neutral chlorine atom as
$\overset{\times\times}{\underset{\times\times}{\times}}\text{Cl}^{\times}_{\times}$, where the crosses represent the seven electrons found in the outermost orbit of chlorine. The fact that we use different symbols to represent the electrons originally associated with the sodium atom and with the chlorine atom does not imply any difference in the nature of these electrons. All electrons are identical, whatever nucleus they may be associated with.

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[1] In the case of helium, the outermost orbit is the first one and can contain only two electrons. This, therefore, represents the stable configuration for the first orbit.

The easiest way in which sodium can attain the stable configuration is to lose the single electron, thereby exposing the next-to-the-outermost orbit, which has eight electrons. The easiest way for chlorine to attain the stable arrangement is to gain one electron. If sodium and chlorine are brought in contact with each other, this is apparently what happens. An electron is transferred from sodium to chlorine, forming the charged ions,

Na^+ and $\overset{\text{x x}}{\underset{\text{x x}}{:Cl:}}^{\text{x}-}$. Strong electrostatic forces between these ions hold them together in a crystal. X-ray examination of this crystal indicates that it is composed of alternate sodium ions and chloride ions but contains no recognizable sodium chloride molecules.

This type of valence is known as *electrovalence*. Compounds held together by it are known as *electrovalent* compounds and show the following general characteristics:

1. They conduct electricity in the fused state.
2. They have high melting points and high boiling points.
3. The unit in their crystal lattice is an ion.
4. They tend to dissolve readily in solvents having a high dielectric constant.

Compounds possessing these characteristics are known as *salts* and include substances like sodium chloride and sodium hydroxide.

The ability of salts to conduct electricity in the fused state may be demonstrated as follows. Place some dry potassium nitrate in an iron crucible, and place a platinum wire so that it is in contact with the salt but not the crucible. If the crucible is connected to one pole of the lighting circuit, and the platinum wire, with a lamp in series with it, to the other pole, no current will flow until the potassium nitrate is melted by heating it. Then the lamp will glow brilliantly.

Covalence. The carbon atom may be pictured as $\cdot\overset{\cdot}{\underset{\cdot}{C}}\cdot$. To reach a stable configuration, this needs to gain four electrons, for those which it already has are too near the nucleus to be lost readily. If carbon is brought in contact with chlorine, we have two elements, each of which needs extra electrons to reach a stable arrangement. Apparently this need can be satisfied by the sharing of a pair of electrons between the two atoms, giving

the following structure for carbon tetrachloride:

$$
\begin{array}{c}
\ _{x}^{xx}Cl_{x}^{x} \\
\ _{x}^{xx}Cl_{x}^{x.\ xx} \ _{x}^{xx}C\ _{.x}^{x}Cl_{x}^{x} \\
\ _{x}^{x}Cl_{x}^{x} \\
xx
\end{array}
$$
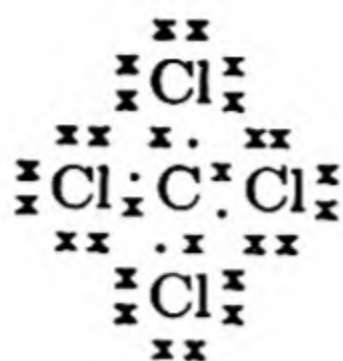
This type of valence is known as *covalence*. Compounds held together by it are known as *covalent* compounds and show the following characteristics:

1. They do not conduct electricity in the fused state.
2. They have low melting points and low boiling points.
3. The unit in their crystal lattice is a molecule. The molecules are held together in the crystal by fairly weak van der Waals forces.
4. They tend to dissolve readily in solvents having a low dielectric constant.

Coordinate Covalence. It will be noticed that, in the case of carbon tetrachloride, each of the elements contributed one electron to the pair that was shared. This is not always the case. Consider ammonia, which has the structure

$$
\begin{array}{c}
H \\
x. \\
H\ _{x}N\ _{.}^{x}H \\
..
\end{array}
$$
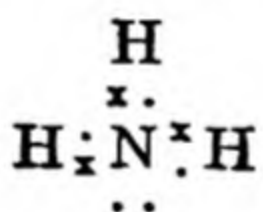
The three hydrogen atoms are held to the nitrogen by covalent bonds, but the nitrogen possesses, in addition, a pair of electrons that is not shared with anything, but that is available if there is anything else that needs two electrons to complete its stable configuration. Such a thing is the proton, H^+, which needs two electrons to reach the stable arrangement of helium. Therefore, if a proton comes in contact with ammonia, it attaches itself, forming the ammonium ion,

$$
\begin{array}{c}
H \qquad + \\
x. \\
H\ _{x}N\ _{.}^{x}H \\
.. \\
H
\end{array}
$$
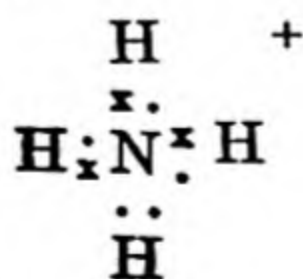
The proton so added is attached by a covalent bond, but one in which both electrons are contributed by one element, in this case

nitrogen. This type of bond is known as *coordinate covalence.*
Another common example of coordinate covalence occurs when a
proton is attached to a water molecule $H\overset{\cdot\cdot}{\underset{\cdot}{\overset{x}{O}}}$ to form the

$$\overset{\cdot}{\underset{H}{\overset{x\cdot}{}}}$$

hydronium ion,

$$H\overset{\cdot\cdot}{\underset{\underset{H}{\overset{x\cdot}{}}}{\overset{x}{O}}}:H \quad \overset{+}{}$$
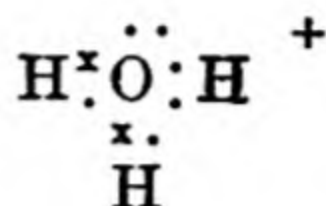
Covalent Compounds Showing Polarity. A good many covalent
compounds are, like carbon tetrachloride, nonpolar; *i.e.*, they are
electrically symmetrical and show no positive and negative poles.
However, this is not always the case. Consider hydrogen
chloride, HCl. This is a covalent compound and shows the
properties of that class of compound, but it does show a definite
polarity. It is as if the shared electrons were more closely asso-
ciated with the chlorine than with the hydrogen, so that the
molecule might better be pictured as

$$+\left(\; H \quad \overset{x}{\underset{\cdot\cdot}{Cl}}\; \right) -$$
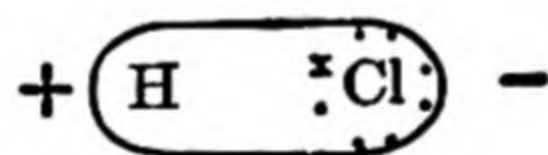
Although this is a molecule and not a pair of ions, it does possess
a positive end and a negative end. Such a molecule is known as
a *dipole.* The extent of its polarity is determined by the magni-
tude of the positive and negative charges and also by the distance
between the charges. The product of these two factors is known
as the *dipole moment* of the molecule.

The dipole moment of the molecules of a substance may be
deduced from measurements of the *dielectric constant* of that
substance as a gas or in solution in a nonpolar solvent. The
dielectric constant of a substance may be defined as the factor
showing the amount by which that substance decreases the
electrostatic force between two charged bodies. The reference
standard is a vacuum, which has a dielectric constant equal to
unity.

The following example may serve to clarify this idea of dielec-
tric constant and also to show its relation to dipole moment.
Figure 6-2*a* represents two oppositely charged plates that are

1 cm. apart and have a vacuum between them. These plates bear a sufficient charge so that the attractive force between them is 80 dynes. Figure 6-2*b* represents the same plates, now separated by water in place of the vacuum. The water molecules are dipoles, and while at first they will have a random distribution they will, under the influence of the electric field, tend to orient themselves as in Fig. 6-2*c*. The fields of these dipoles are now opposed to the fields of the plates and tend to neutralize them. This decreases the attraction that the plates have for each other. The extent of this effect depends in part upon the dipole moment of the molecules. Under the new conditions, the attractive force between the plates is found to be only 1 dyne instead of 80 dynes. Therefore, we say that the dielectric constant of water is 80.[1]
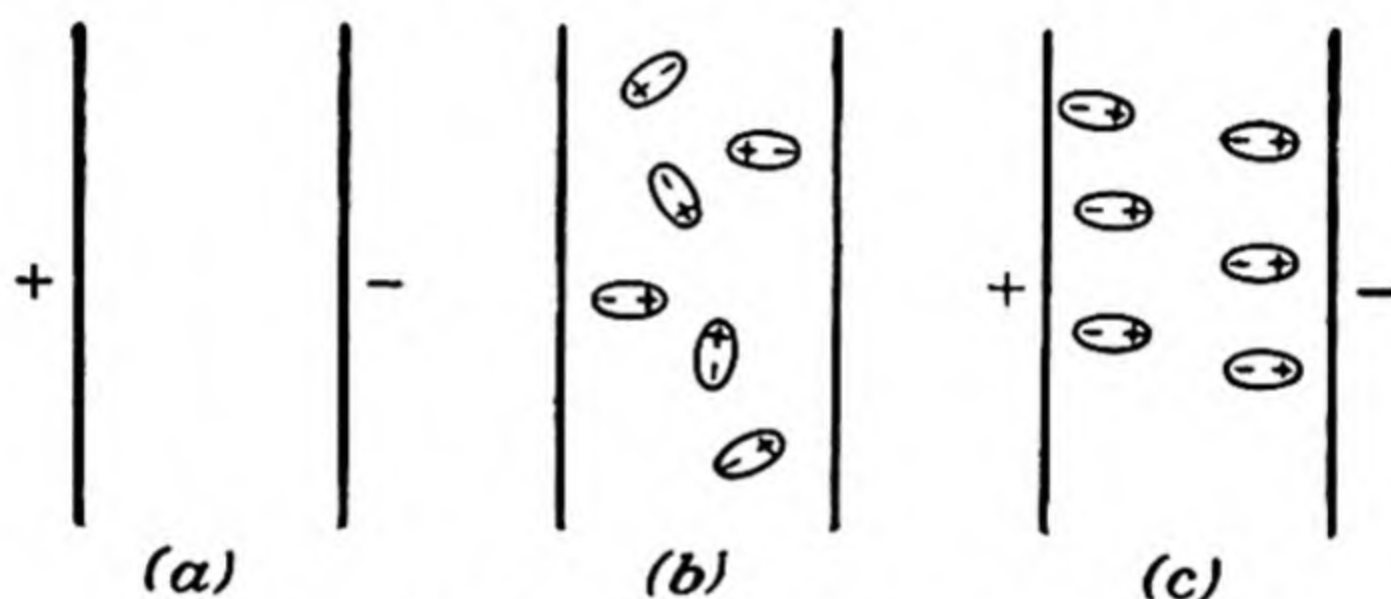
FIG. 6-2. The dielectric effect of polar molecules.

Table 6-4 gives the dipole moments and dielectric constants of a few substances. It will be noted that molecules that are electrically symmetrical have a dipole moment of zero and a low dielectric constant. The reason that carbon tetrachloride and benzene have dielectric constants slightly greater than unity is that when these substances are placed between charged plates the electric field between the plates causes a slight shift in the distribution of the electrons around the molecule, thus making the molecule temporarily a dipole. This *induced polarization* disappears when the electric field is removed. Induced polarization accounts in part for the lack of exact correspondence, indicated in Table 6-4, between the values of the dipole moments of the various substances and their dielectric constants in the liquid state.

[1] For a discussion of the methods by which dipole moments may be determined, see S. Glasstone, "Textbook of Physical Chemistry," 2d ed., pp. 546–551, D. Van Nostrand Company, Inc., New York, 1946.

TABLE 6-4. DIPOLE MOMENTS AND DIELECTRIC CONSTANTS OF SOME SUBSTANCES

Substance	Dipole moment e.s.u. $\times$ cm. $\times 10^{18}$	Dielectric constant of liquid
Carbon tetrachloride.......	0	2.24
Benzene.................	0	2.28
Hydrogen chloride........	1.03	4.6
Ammonia................	1.44	15.5
Phenol..................	1.56	10.6
Ethyl alcohol.............	1.7	25.8
Methyl alcohol...........	1.7	31.2
Water..................	1.87	80

Molecules having dipoles tend to cling together, the positive portion of one being attracted to the negative portion of another. Thus, polar molecules can form more or less stable unions, not only among themselves, but with other polar substances. They may also induce polarity in nonpolar molecules. As a result, it is found that polar substances are chemically reactive and that polar liquids are usually associated and are good ionizing solvents.

The Hydrogen Bond. The attraction between molecules having dipoles is especially great when hydrogen, attached to oxygen, nitrogen, or halogen, is present. This is so because, under these conditions, the electrical fields around the hydrogen are particularly strong and concentrated and exert a powerful attraction on unshared electrons in other molecules. This enables hydrogen to link together two strongly electronegative elements and the molecules containing them. Such systems are said to exhibit *hydrogen bonding.*

Originally, hydrogen bonding was explained on the assumption that the hydrogen atom was able to form two covalent bonds. It is now recognized, however, that hydrogen is incapable of forming two such covalences, and that the hydrogen bond is due primarily to the electrostatic attraction of a proton for two negative groups. A hydrogen bond has never been found to link more than two atoms. This is probably due to the extremely small size of the hydrogen nucleus.

Hydrogen bonding has been used to explain the formation of the bifluoride ion, HF_2^-, and is believed to be responsible for the

association of water, and similar liquids, into double molecules or larger aggregates. Some of the unusual physical properties of water, liquid ammonia, alcohols, etc., may be accounted for on the basis of the hydrogen bond.

EFFECT OF SOLVENT ON DIFFERENT TYPES OF COMPOUNDS

On Electrovalent Compounds. When a salt, such as sodium chloride, is placed in contact with water, the dipole molecules of water exert a strong attraction on the ions, the positive end of the dipole being attracted to the negative chloride ion, and the negative end of the dipole being attracted to the positive sodium ion. This process is known as *hydration* of the ions and releases energy known as *energy of hydration*. The extent to which the attraction of water molecules for ions is able to overcome the attraction between oppositely charged ions, or in other words, the extent to which the energy of hydration is able to overcome the lattice energy which holds the ions in the crystal, largely determines the extent to which ions leave the crystal, *i.e.*, the extent to which the salt dissolves.

In solution, the ions have attached to them an indeterminate number of water molecules, somewhat as follows:
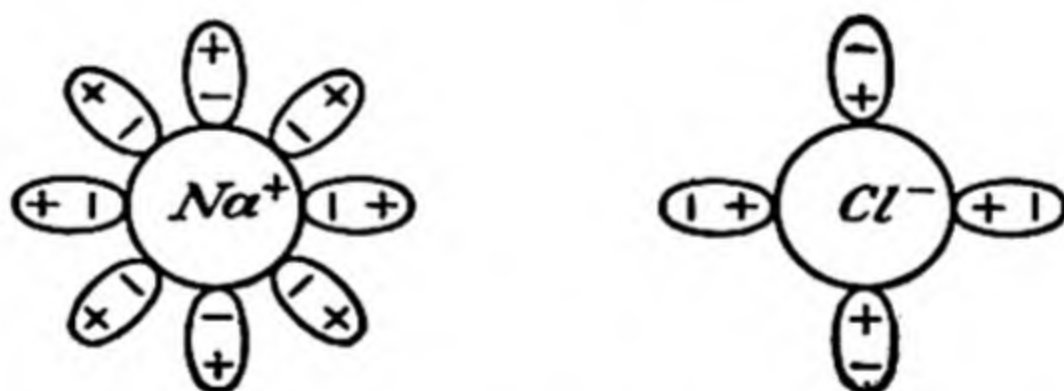
There is some evidence to indicate that the sodium ion has attached to it about twice as many water molecules as does the chloride ion.[1] These water dipoles are quite firmly attached to the ions. This, plus the fact that the high dielectric constant of water diminishes the attraction between the oppositely charged ions, decreases their tendency to unite to re-form the crystal. Therefore, a considerable quantity of the salt dissolves and is present in the solution entirely in the form of ions. No test which has yet been applied has disclosed the presence of sodium chloride molecules in the solution, nor is there any reason to

[1] WASHBURN, E. W., *J. Am. Chem. Soc.*, **31**, 322 (1909).

believe that any exist. The solution is an excellent conductor of electricity.

Although there are exceptions, it may be stated in general that electrovalent compounds will dissolve in polar solvents, such as water, whose molecules will attach themselves to the ions of the compounds, *i.e.*, will solvate them. On the other hand, nonpolar solvents, such as benzene, will not solvate the ions of a salt and hence no energy of solvation is supplied to overcome the lattice energy of the salt. Accordingly the salt has little tendency to dissolve in this type of solvent.

The reason that some electrovalent compounds, as for example, barium sulfate, have a very slight solubility in water is that the lattice energy holding the barium and sulfate ions in the crystal is so great that the energy supplied by the process of hydration is inadequate to overcome it.

On Nonpolar Covalent Compounds. A covalent compound, such as carbon tetrachloride, which shows no polarity, dissolves only slightly in polar solvents, such as water, but dissolves readily in solvents, like ether, that are nonpolar. In no case will carbon tetrachloride ionize, and its solutions do not conduct electricity.

We may picture this behavior of carbon tetrachloride in water and in ether as follows: The water molecules, being dipoles, exert some attraction for each other. This holds them together in a compact arrangement and affords little opportunity for the carbon tetrachloride molecules to diffuse into the water. In the case of ether, no such attraction exists, and the carbon tetrachloride molecules can diffuse readily in among the ether molecules.

On Polar Covalent Compounds. A covalent compound, such as hydrogen chloride, that shows polarity, may sometimes dissolve in both polar and nonpolar solvents. The properties of the resulting solution will depend on the nature of the solvent.

If hydrogen chloride is dissolved in the nonpolar solvent toluene, the solution will not conduct electricity. Apparently the solute exists only as molecules of hydrogen chloride.

If, however, hydrogen chloride is dissolved in water or ammonia, both polar solvents, the solution is an excellent conductor of electricity and gives evidence that the solute is completely converted into ions.

The explanation advanced by Brønsted to explain these facts

is as follows: It will be recalled that water and ammonia, in addition to being polar solvents, each possess an unused pair of electrons that is capable of forming a coordinate covalence with a proton. If the attraction of the solvent for protons is sufficiently strong then there will occur between solute and solvent an exchange of protons, or a *protolytic reaction*, resulting in the formation of positive and negative ions.

$$H_2O + HCl \rightleftharpoons H_3O^+ + Cl^-$$
$$NH_3 + HCl \rightleftharpoons NH_4^+ + Cl^-$$
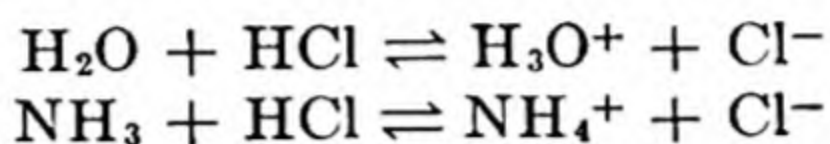
If, on the other hand, the attraction of the solute for protons is sufficiently great, protons will be transferred from solvent to solute, again resulting in the formation of ions. An example of this protolysis is the reaction of ammonia in solution in water.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
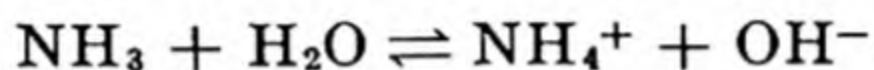
On the basis of the above types of reactions, Brønsted has proposed the following definitions of acid and base. An *acid* is a *proton donor;* a *base* is a *proton acceptor.* In the reactions involving hydrogen chloride, that substance acts as an acid, while water and ammonia act as bases. In the reaction between ammonia and water, the former is a base, the latter is an acid.

Substances other than water which exhibit basic properties because they contain an oxygen atom with an unshared pair of electrons are alcohols, ethers, and ketones. The ability of these substances to accept protons may be demonstrated in the following way: In each of three test tubes put about 10 ml. of anhydrous chlorobenzene. To each add 3 or 4 drops of a solution of methyl violet in chlorobenzene. Methyl violet turns yellow when protons are added to it and turns back to violet when these protons are removed. Now add to each test tube a few drops of anhydrous trichloracetic acid, and note the change in color of the methyl violet. Now add to one test tube anhydrous ethyl alcohol, to a second anhydrous ethyl ether, to the third anhydrous acetone. In each case note the change in color as the added base removes the protons from the methyl violet.

In water solution, acids produce hydronium ions, H_3O^+, which confer upon the solution the properties we commonly associate with acids, such as sour taste and ability to turn blue litmus red. Similarly, bases produce hydroxide ions, OH^-, which have the

properties associated with bases, such as bitter taste and ability to turn red litmus blue. The base that is formed by the removal of a proton from an acid is called *conjugate* to the acid.

CONJUGATE ACIDS AND BASES

Acid	Base
HCl	Cl^-
H_2O	OH^-
H_3O^+	H_2O
NH_4^+	NH_3
HCO_3^-	CO_3^{--}

It will be noted that the protolytic reactions already cited consist of the reaction of an acid and a base to form a new acid and base, which are conjugate to the original ones. Therefore a type formula may be written for protolytic reactions as follows. The acid and base having the same subscript are conjugate.

$Acid_1$	+	$base_2$	$\rightleftharpoons$	$acid_2$	+	$base_1$
HCl	+	H_2O	$\rightleftharpoons$	H_3O^+	+	Cl^-
H_2O	+	NH_3	$\rightleftharpoons$	NH_4^+	+	OH^-
HCO_3^-	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CO_3^{--}
H_2O	+	CO_3^{--}	$\rightleftharpoons$	HCO_3^-	+	OH^-
H_2O	+	H_2O	$\rightleftharpoons$	H_3O^+	+	OH^-
HCl	+	NH_3	$\rightleftharpoons$	NH_4^+	+	Cl^-

The extent to which the protolytic reaction between solute and solvent proceeds determines what we ordinarily call the *degree of ionization* of the solute. It is obvious that this depends not only on the nature of the solute, but also on that of the solvent. Acetic acid is a weak proton donor. If acetic acid is dissolved in water, which is a weak proton acceptor, the protolytic reaction goes on only to a slight extent. We say that acetic acid is only slightly ionized in water solution. If, on the other hand, acetic acid is dissolved in liquid ammonia, which is a better proton acceptor than is water, the protolytic reaction will go on to a greater extent. In other words, acetic acid is considerably ionized in ammonia solution. It will be of value to be able to determine the extent of these protolytic reactions when water is the solvent, *i.e.*, to determine the degree of ionization of the solute in aqueous solution.

DEGREE OF IONIZATION

Of Strong Electrolytes. It has already been stated that in water solutions of salts, such as potassium chloride, there is no evidence of the existence of molecules of the solute, and the belief is that they are completely dissociated into ions. This is also true of dilute solutions of the strong acids, such as hydrogen chloride.

Each molecule of the solutes mentioned above is converted into two ions. Therefore, if Arrhenius' theory is correct, we should expect the value of i for solutions of these solutes to be 2.0 at all concentrations. Actually, as shown in Table 6-1, i reaches this value only in extremely dilute solutions. The question then arises as to why the value of i, at finite concentrations, is less than its maximum value.

The answer to this question that has been proposed by Debye and Hückel is that the force of interionic attraction existing between oppositely charged ions hinders their independence of action and so makes their *effective concentration* less than their *actual concentration*. It is the effective concentration that determines the value of i. This effective concentration is called the *activity* of the ion. The symbol for activity is a.

For the relation between activity and concentration the student should refer to the discussion of activity in Chap. 5. The relations there established apply to ions as well as to other solutes.

The force of interionic attraction varies with the charges on the ions and inversely as the square of the distance between them in the solution. The combined effect of these factors is expressed as the ionic strength, μ, of the solution. The ionic strength may be calculated by the following equation:

$$\mu = 0.5\Sigma(mz^2) \tag{6-5}$$

in which Σ indicates a summation of the term mz^2 for each kind of ion present in the solution, m is the molality of the ion, and z is its valence.

Example. What is the ionic strength of a solution that contains $0.002m$ potassium chloride and $0.001m$ calcium chloride?

$$m_{K^+} = 0.002 \qquad m_{Ca^{++}} = 0.001 \qquad m_{Cl^-} = 0.004$$
$$\mu = 0.5[(0.002 \times 1^2) + (0.001 \times 2^2) + (0.004 \times 1^2)] = 0.005$$
$$K^+ \qquad\qquad\quad Ca^{++} \qquad\qquad\quad Cl^-$$

In aqueous solutions whose ionic strength is not greater than 0.01, the effect that the ionic strength has, at 25°C., on the activity coefficient of each ion is given by the expression

$$\log \gamma = -0.5z^2 \sqrt{\mu} \qquad\qquad (6\text{-}6)$$

where z represents the valence of the ion in question.

Example. Calculate the activity coefficients and the activities of the ions in the preceding example.

$$\log \gamma_{K^+} = \log \gamma_{Cl^-} = -0.5 \times 1^2 \sqrt{0.005} = -0.035$$
$$\gamma_{K^+} = \gamma_{Cl^-} = \text{antilog} \; -0.035 = 0.92$$
$$\log \gamma_{Ca^{++}} = -0.5 \times 2^2 \sqrt{0.005} = -0.14$$
$$\gamma_{Ca^{++}} = \text{antilog} \; -0.14 = 0.72$$
$$a_{K^+} = 0.92 \times 0.002 = 0.0018$$
$$a_{Cl^-} = 0.92 \times 0.004 = 0.0037$$
$$a_{Ca^{++}} = 0.72 \times 0.001 = 0.00072$$

As the solutions become more dilute, the force of interionic attraction decreases and the ions are able to act more independently of each other. At infinite dilution the activity equals the concentration. At this point i shows its maximum value.

Of Weak Electrolytes. In the case of water solutions of weak electrolytes, such as acetic acid or ammonia, the protolytic reaction has gone on only to a very limited extent. Therefore, the concentration of the ions and the ionic strength of the solution are very small. Consequently, we may say, without any considerable error, that the activity of the ions is approximately equal to their concentration, even in fairly concentrated solutions.

If this is so, then the variations in the value of i for these weak electrolytes must be caused by actual variations in the degree of ionization, rather than by the force of interionic attraction. If then we can establish a relationship between i and the degree of ionization, we shall have a means of calculating the latter.

This relationship can be established as follows, remembering that the value of i depends upon the total number of solute particles, both molecules and ions, present in the solution. Starting, for convenience, with 1 mole of solute, let α represent the degree of ionization, *i.e.*, the fraction of this mole that is converted into

ions.   Let n represent the number of ions formed when 1 molecule of solute is ionized.   As a result of the ionization, $(1 - \alpha)$ mole of solute will be left in the un-ionized state, and $n\alpha$ moles of ions will be formed.   Therefore, the total number of moles of both un-ionized molecules and ions present in the solution will be

$$1 - \alpha + n\alpha = 1 + (n - 1)\alpha$$

It has been shown that any of the colligative properties of solutions, such as the freezing-point depression, is determined by the total number of moles of solute present in the solution. Therefore, if no ionization had taken place, the freezing-point depression of this solution would be the same as the normal freezing-point depression of a solution containing 1 mole of a nonelectrolyte.   As a result of ionization, the actual freezing-point depression of the solution would be equal to the normal value multiplied by the total number of moles of both molecules and ions present, *i.e.*, by $1 + (n - 1)\alpha$.   From these relationships we can derive the following expression for i:

$$i = \frac{\text{observed freezing-point depression}}{\text{normal freezing-point depression}} = 1 + (n - 1)\alpha \quad (6\text{-}7)$$

This equation is valid for any number of moles of solute, for if some number of moles, x, not equal to 1 had been taken, it would simply mean multiplying both numerator and denominator of the expression by x, and these values of x would cancel each other.

Equation (6-7) may be solved for α to give

$$\alpha = \frac{i - 1}{n - 1} \quad\quad (6\text{-}8)$$

Example.   The freezing point of $0.1m$ acetic acid is $-0.188°C$.   Calculate the degree of ionization of acetic acid in 0.1 molal solution.   Acetic acid ionizes to give two ions per molecule.   Therefore, $n = 2$.

$$i = \frac{0.188}{0.186} = 1.01 \quad\quad \alpha = \frac{1.01 - 1}{2 - 1} = 0.01$$

Electrical Conductance of Solutions

Another commonly used method for determining the degree of ionization of a solute is to measure the *conductance* of its solution. The conductance of a solution is its ability to carry an electric current, or the rate at which electricity flows through it under

unit difference of potential. Conductance is the reciprocal of resistance and is measured in *reciprocal ohms*. The symbol that we shall use for reciprocal ohms is simply the word "ohm" spelled backward.

$$\text{Reciprocal ohms} = \text{mhos} = \frac{1}{\text{ohms}} = \frac{\text{amp.}}{\text{volts}} \qquad (6\text{-}9)$$

Since electricity is carried through the solution only by the migration of the ions, and none of it by the molecules, it might be possible to use conductance data to calculate the number of ions present in a solution and hence the degree of ionization of the solute.

The conductance of a solution is determined by the number of positive and negative charges that reach the electrodes per second. This will be affected by the following factors:

1. The number of positive and negative charges present. This will be determined by
   a. The number of ions present.
   b. The charge on each ion.
2. The speed of the ions. This will be determined by
   a. The voltage between the electrodes.
   b. The temperature.
   c. The mobility of the ions.
   d. The force of interionic attraction.
3. The distance between the electrodes.

It will be convenient, when comparing the conductances of various solutes, to take as the standard amount of solute that quantity which will always give the same number of positive charges, and of negative charges, when completely ionized. A quantity satisfying these requirements is the gram-equivalent. If a sufficient volume of solution is taken so that it contains 1 gram-equivalent of solute, and if this volume is contained between electrodes that are 1 cm. apart, the conductance of the solution under these conditions is known as its *equivalent conductance* and is indicated by the Greek capital letter lambda Λ.

Suppose, for example, that we wished to measure the equivalent conductance of potassium chloride. We might take 1 gram-equivalent (74.56 g.) of that salt and place it between the elec-

trodes indicated in Fig. 6-3. We could then add enough water to make 1 liter of solution. This would be a normal solution, and the conductance measured would be the equivalent conductance of 1N potassium chloride. This conductance would be designated as Λ_1. The subscript numeral in this case indicates the normality of the solution. If now enough more water is added to make the volume 10 liters, the conductance measured will be that of 0.1N potassium chloride and will be indicated by $\Lambda_{0.1}$.

It would obviously be inconvenient to construct an electrode vessel large enough to contain 1 gram-equivalent of solute in a dilute solution. (For a 0.001 normal solution, each electrode would have to be 10 meters square.) Fortunately this is not necessary. The value of the equivalent conductance can be calculated by measuring the conductance of a 1-cm. cube of the solution and multiplying this value by the number of cubic centimeters of the solution required to contain 1 gram-equivalent of the solute. The conductance of a 1-cm. cube of solution is known as the *specific conductance* of that solution. Specific conductance is usually designated by the Greek letter kappa κ.
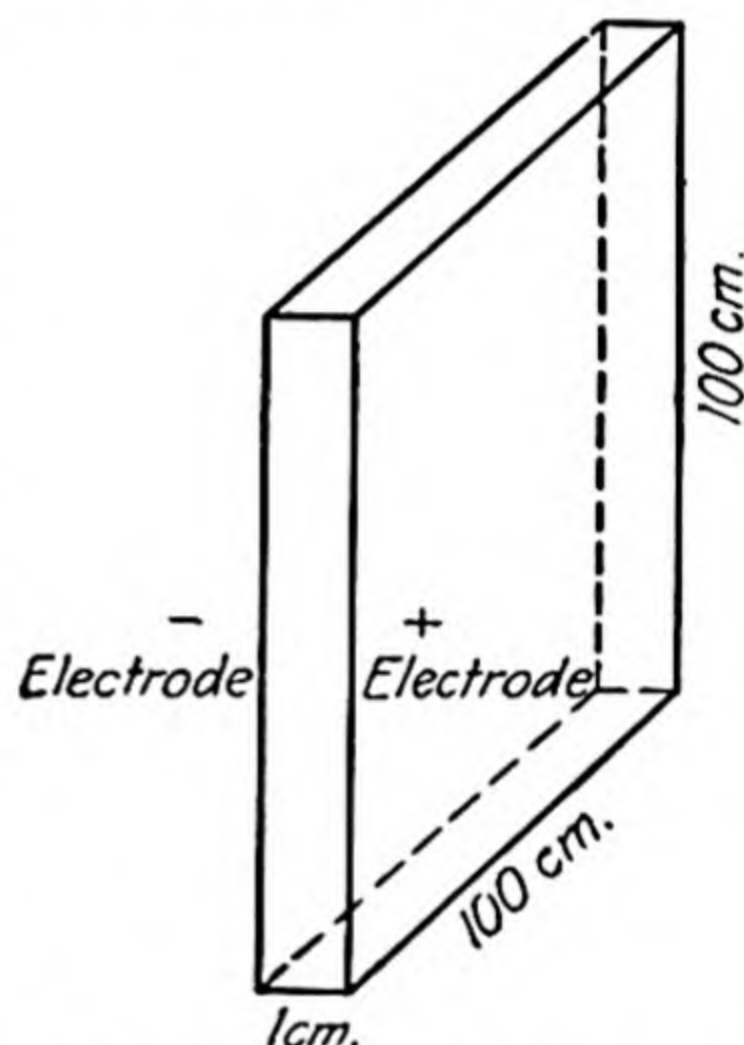
FIG. 6-3. Container for measuring the equivalent conductance of a solution.

$\Lambda = \kappa \times$ volume in cubic centimeters containing

$$1 \text{ gram-equivalent of solute} \quad (6\text{-}10)$$

Example. The equivalent conductance of 0.1M potassium chloride, KCl, is equal to 10,000 times its specific conductance. On the other hand, the equivalent conductance of 0.1M calcium chloride, CaCl$_2$, is only 5,000 times its specific conductance.

As a solution becomes more and more dilute, the value of the specific conductance decreases, but that of the equivalent conductance increases to a maximum.

Experimental Determination of Conductance. One type of cell in which the conductance of a solution may be measured is

TABLE 6-5. SPECIFIC AND EQUIVALENT CONDUCTANCES, IN MHOS, OF POTASSIUM CHLORIDE, AT 25°C.

Normality	κ	Λ
1.0	0.1119	111.9
0.1	0.01289	128.9
0.01	0.001413	141.3
0.001	0.0001469	146.9
0.0001	0.00001489	148.9
0.0000	. . . .	149.9

illustrated in Fig. 6-4.   It consists of a small glass bottle in which the solution is placed.   Extending into this bottle are two glass tubes, to the lower ends of which are sealed squares of platinized platinum.   These squares are kept a fixed distance apart by means of glass rods.   When the tubes are filled with mercury, contact may be made with an outside circuit by inserting wires into the open upper ends of the tubes.
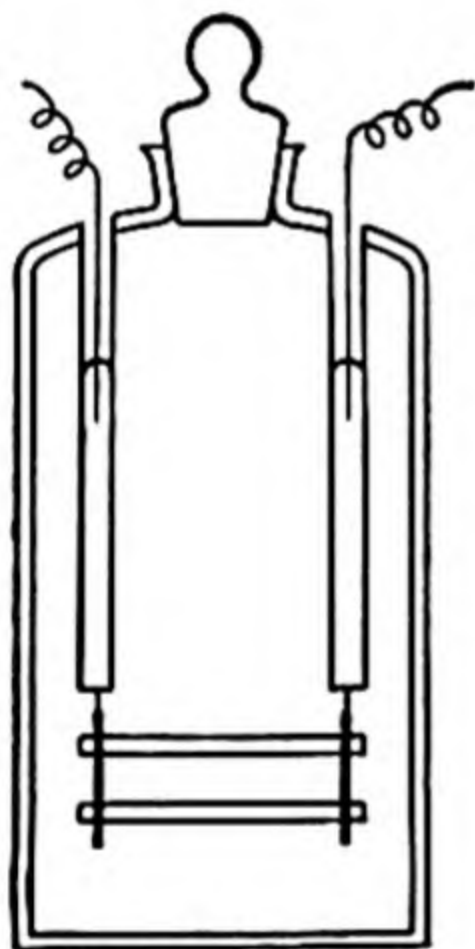
FIG. 6-4.   One type of conductance cell.

The platinum electrodes may not be exactly 1 cm.² in area and 1 cm. apart.   If this is the case, the conductance measured will not be the specific conductance of the solution, for conductance varies directly as the area of the electrodes, inversely as the distance between them.   To calculate the value of the specific conductance, it will be necessary to multiply the observed conductance by a constant c.

This constant c is known as the *cell constant*, and its value depends on the size and distance apart of the electrodes in the cell.

$$\kappa = \text{observed conductance} \times c \qquad (6\text{-}11)$$

The value of the cell constant for a particular cell can be determined by measuring, in that cell, the conductance of a solution whose specific conductance is known.

$$c = \frac{\text{specific conductance}}{\text{observed conductance}} \qquad (6\text{-}12)$$

Example. The observed conductance of 0.1N potassium chloride in a cell, at 25°C., is 0.020 mho. Calculate the value of the cell constant.

$$c = \frac{0.01289}{0.020} = 0.64$$

Since conductance is the reciprocal of resistance, the observed conductance of a solution may be determined by comparing the resistance of the solution with a known resistance. This comparison may be made by using the type of apparatus illustrated in Fig. 6-5. In this figure, E represents a microphone hummer, or other source of high-frequency alternating current. (The use of
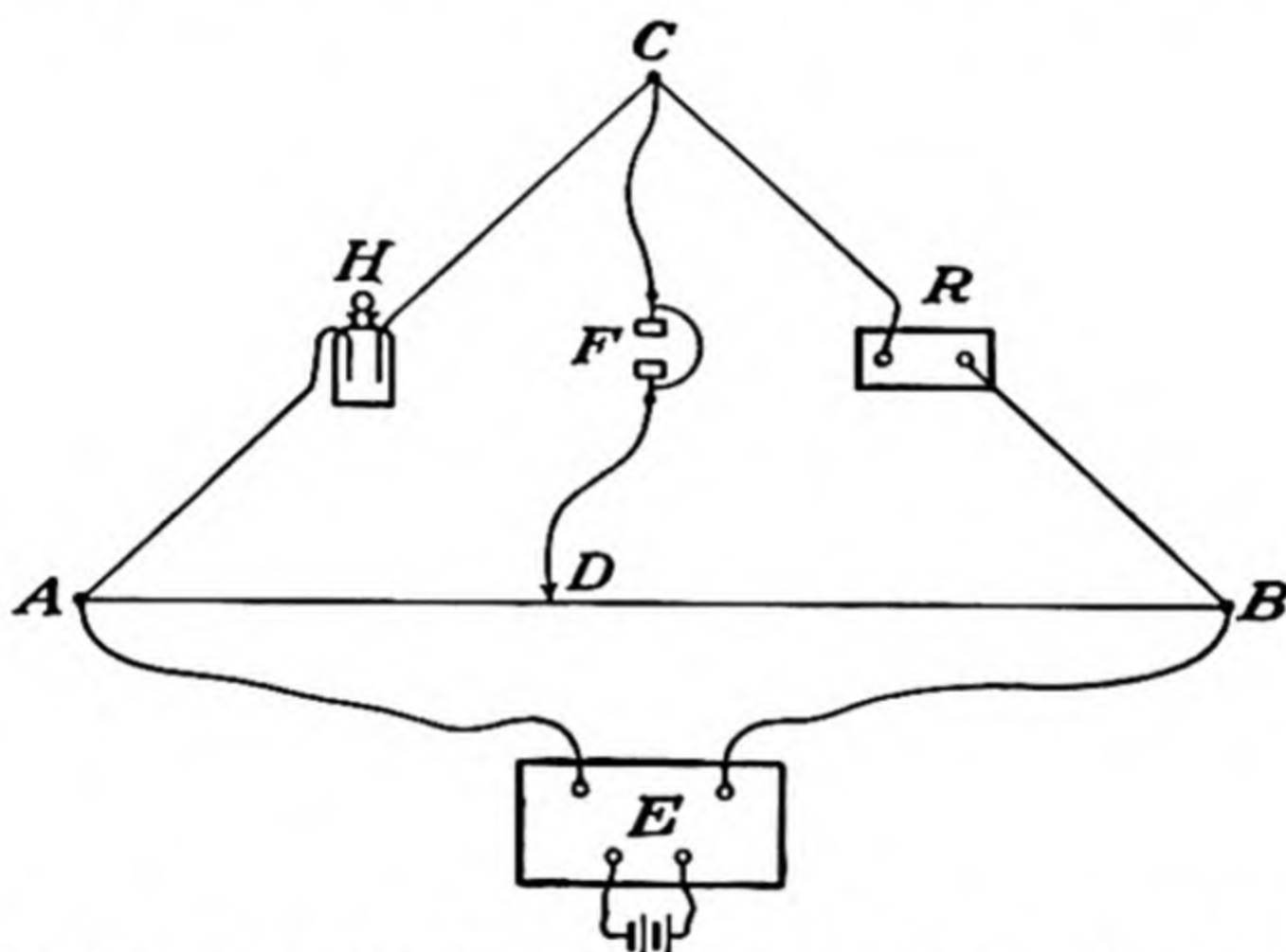
FIG. 6-5. Apparatus for measuring the resistance of a solution.

direct current would introduce complications due to electrolysis of the solution.) AB is a wire of uniform resistance, usually 1 m. in length, and graduated in millimeters. H is the conductance cell, holding the solution whose resistance is to be measured. R is a resistance box, furnishing a known resistance which may be varied in steps. F is a telephone receiver, and D is a movable contact.

The current flowing between A and B will travel along two paths ADB and ACB. The potential difference between any two points along either circuit is proportional to the fraction of the total resistance of the circuit that is encountered between those two points. Since AB is wire of uniform resistance, the resistance between A and D is the following fraction of the total

resistance of the wire, AD/AB. Let us assume that along the circuit ACB the resistance of the connecting wires is negligible and, therefore, the only resistances to be considered are those encountered in the cell H and in the known resistance R. Let x represent the resistance of the solution in the cell H. Then the resistance between A and C is the following fraction of the total resistance along the circuit $x/(x + R)$. If the potential drop between A and D equals that between A and C, no current will flow between C and D, and the telephone receiver will be silent. If the two potential drops are not the same, current will flow between C and D and the sound of the hummer will be heard in the receiver. This sound will become louder as the potential difference between C and D increases. At the silent point

$$\frac{AD}{AB} = \frac{x}{x + R}$$

The above expression, when solved for x, gives

$$x = \frac{AD}{AB - AD} \times R \qquad (6\text{-}13)$$

In practice, a known resistance is set up in R, and the contact D is moved until no sound is heard in the receiver. Then the values for AB, AD, and R are substituted in Eq. (6-13) to give the resistance of the solution in the conductance cell.

Example. From the following data, calculate the equivalent conductance for $0.1N$ sodium nitrate. The cell constant for the cell used was 0.430. The value of R was 40.0 ohms. At the silent point, AD was 552 mm. The distance AB was $1,000$ mm.

$$x = \frac{552}{1,000 - 552} \times 40.0 = 49.2 \text{ ohms}$$

$$\text{Observed conductance} = \frac{1}{49.2} = 0.0203 \text{ mho}$$

$$\text{Specific conductance} = 0.0203 \times 0.430 = 0.00872 \text{ mho}$$

$$\text{Equivalent conductance} = 0.00872 \times 10,000 = 87.2 \text{ mhos}$$

In Fig. 6-6 the values for the equivalent conductance of potassium chloride from Table 6-5 are plotted against the square root of the normality of the solution. At low concentrations the curve so formed becomes nearly linear and approaches the vertical axis at nearly a right angle. Under these conditions the short

extrapolation (dotted line) to zero concentration can be made with considerable accuracy. This extrapolated value of 149.9 mhos, at zero concentration, is known as the equivalent conductance of the salt at infinite dilution, and is designated by Λ_∞.

The type of curve shown for potassium chloride in Fig. 6-6 is characteristic of salts and other strong electrolytes. Since these are believed to be completely ionized at all dilutions and since, in
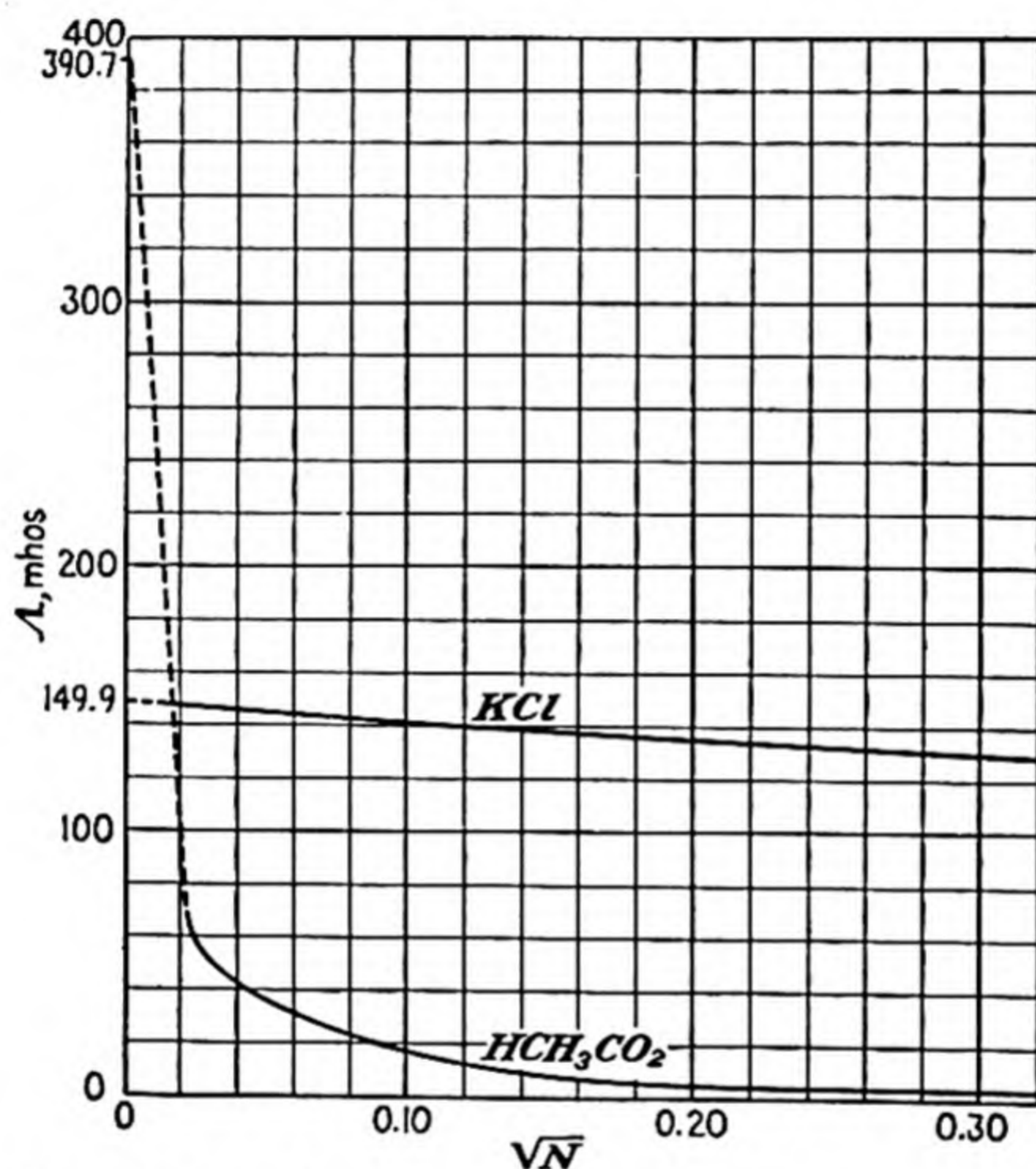
FIG. 6-6. Equivalent conductances of potassium chloride and acetic acid solutions, at 25°C., plotted against the square root of their normalities.

the determination of the equivalent conductance, all the factors affecting it were kept constant except the force of interionic attraction, it is believed that variations in the value of the equivalent conductance are caused by changes in the force of interionic attraction, which affect the speed of the ions. At infinite dilution, the force of interionic attraction is negligible. Therefore, at this dilution each ion is capable of independent action and shows its true conductance. The equivalent conductance of the solution at infinite dilution is the sum of the equivalent con-

ductances at infinite dilution of its component ions.

$$\Lambda_\infty = \lambda_{c,\infty} + \lambda_{a,\infty} \qquad (6\text{-}14)$$

In Eq. (6-14) $\lambda_{c,\infty}$ represents the conductance at infinite dilution of 1 gram-equivalent of cation; $\lambda_{a,\infty}$ represents the conductance at infinite dilution of 1 gram-equivalent of anion.

Ionic Conductances. The equivalent conductances of a typical weak electrolyte, acetic acid, at various normalities are given in Table 6-6. These values are plotted against the square root of the normality in Fig. 6-6. In this case the curve, at the lowest concentration for which data are given, has not become linear; also it approaches the vertical axis at an oblique angle. Both of these circumstances mean that extrapolation to zero concentration is subject to large errors. In such cases the value of the equivalent conductance at infinite dilution must be determined indirectly.

TABLE 6-6. EQUIVALENT CONDUCTANCE, IN MHOS, OF ACETIC ACID, AT 25°C.

Normality	Λ
0.1	5.2
0.01	16.3
0.001	49.2
0.0005	67.7
0.0000	390.7

The indirect determination of the equivalent conductance at infinite dilution of substances like acetic acid is made possible by the fact, already mentioned, that a gram-equivalent of an ion has a definite conductance. Each ion has its own particular equivalent conductance at infinite dilution, and the value of this is independent of the compound from which the ion is obtained. Thus the equivalent conductance at infinite dilution of potassium ion is the same whether the ion is obtained from potassium chloride, potassium hydroxide, or potassium sulfate. The equivalent conductance at infinite dilution of any electrolyte is equal to the sum of the equivalent conductances at infinite dilution of its ions. The use of these facts is illustrated in the following determination of the equivalent conductance at infinite dilution of acetic acid. Hydrochloric acid, potassium acetate, and potassium chloride are all strong electrolytes, and the equivalent conductances at infinite dilution of these substances, at 25°C.,

can be obtained directly from their curves with the following results:

$$HCl, \Lambda_\infty = \lambda_{H_3O^+,\infty} + \lambda_{Cl^-,\infty} = 426.1 \text{ mhos}$$
$$KCH_3CO_2, \Lambda_\infty = \lambda_{K^+,\infty} + \lambda_{CH_3CO_2^-,\infty} = 114.5 \text{ mhos}$$
$$KCl, \Lambda_\infty = \lambda_{K^+,\infty} + \lambda_{Cl^-,\infty} = 149.9 \text{ mhos}$$

If the equivalent conductance at infinite dilution of potassium chloride is subtracted from the sum of the equivalent conductances at infinite dilution of hydrochloric acid and potassium acetate, it is found that the remainder is

$$\lambda_{H_3O^+,\infty} + \lambda_{CH_3CO_2^-,\infty} = 390.7 \text{ mhos}$$

which is the equivalent conductance at infinite dilution of acetic acid, at 25°C.

In solutions of weak electrolytes, such as acetic acid, it is assumed that the force of interionic attraction is very slight, even in fairly concentrated solutions. Therefore, variations in the value of the equivalent conductance are attributed to actual changes in the number of ions present, or to changes in the degree of ionization. If this idea is accepted, then we can say that the equivalent conductance at infinite dilution corresponds to complete ionization. At finite concentrations the degree of ionization is given by the expression

$$\alpha = \frac{\Lambda_c}{\Lambda_\infty} \qquad (6\text{-}15)$$

where Λ_c represents the equivalent conductance at the particular concentration in question.

Example. From the data in Table 6-6, calculate the degree of ionization of $0.1N$ acetic acid.

$$\alpha = \frac{\Lambda_{0.1}}{\Lambda_\infty} = \frac{5.2}{390.7} = 0.013 = 1.3 \text{ per cent}$$

Transference Numbers. Values for the equivalent conductances at infinite dilution of individual ions could be calculated if we had some means of ascertaining what fraction of the equivalent conductance of an electrolyte at infinite dilution could be attributed to each of its ions. This fraction is known as the *transference number* of the ion and is designated as t_c for the cation and t_a for the anion. The sum of the transference numbers of cation and

anion for any electrolyte equals unity.

$$t_c + t_a = 1 \qquad (6\text{-}16)$$

It has been stated that one of the factors affecting the conductance of a solution is the *mobility* of its ions. Mobility is defined as the speed of migration of the ion, in centimeters per second, under a potential drop of 1 volt/cm. If all ions moved with the same speed, the equivalent conductances at infinite dilution of all electrolytes would be the same, because there would be the same number of coulombs per second passing through the solution, and the transference numbers of cation and anion in all electrolytes would be 0.5, because each ion would carry half the current. Experience has shown that the equivalent conductances at infinite dilution vary widely for different electrolytes. From this we conclude that the ions move at different speeds, or have different mobilities.

The transference numbers of the cation and anion in an electrolyte can be deduced from measurements of the changes in concentration around the anode and the cathode during the electrolysis of that electrolyte.[1] For any particular cation the value of the transference number varies with the anion with which it is combined. Transference numbers for the ions of a particular electrolyte also vary with concentration, and transference numbers at infinite dilution may be obtained by plotting transference number against the square root of the normality and extrapolating the curve to zero concentration.

The equivalent conductance of an ion at any particular concentration is equal to the equivalent conductance of the electrolyte containing that ion multiplied by the transference number of the ion in that electrolyte, both at the same concentration.

Table 6-7 gives the equivalent conductances at infinite dilution of some ions at 25°C. These were obtained by multiplying the equivalent conductances at infinite dilution of electrolytes containing these ions by the transference numbers at infinite dilution of the ions in those electrolytes.

$$\lambda_{c,\infty} = t_{c,\infty}\Lambda_\infty \qquad (6\text{-}17)$$
$$\lambda_{a,\infty} = t_{a,\infty}\Lambda_\infty \qquad (6\text{-}18)$$

[1] See S. GLASSTONE, "Textbook of Physical Chemistry," 2d ed., p. 910, D. Van Nostrand Company, Inc., New York, 1946.

TABLE 6-7. EQUIVALENT CONDUCTANCES AND MOBILITIES OF SOME IONS
AT INFINITE DILUTION AND AT 25°C.

Cation	$\lambda_{c,\infty}$ mhos	Mobility, cm./sec.	Anion	$\lambda_{a,\infty}$ mhos	Mobility, cm./sec.
Hydronium......	349.8	0.00362	Hydroxide.......	197.6	0.00205
Potassium.......	73.5	0.00076	Sulfate..........	79.8	0.00083
Ammonium......	73.4	0.00076	Chloride........	76.3	0.00079
Calcium.........	59.5	0.00062	Nitrate.........	71.4	0.00074
Magnesium......	53.1	0.00055	Acetate.........	40.9	0.00042
Sodium..........	50.1	0.00052			

Ionic Mobilities.   The mobilities of the ions can be determined by direct observation in the *moving boundary* method or they can be calculated from the equivalent conductances of the ions.   The results of the two methods are in satisfactory agreement.

Moving-boundary Method.   If an ion confers some observable physical property, such as color or refractive index, on a solution, it is sometimes possible to follow the progress of the ion through the solution and to measure its velocity.   A solution of one electrolyte is carefully floated on top of another in a long vertical tube of uniform diameter, so that the boundary between the two solutions is sharp and observable.   If a potential is imposed on the solutions the motion of the boundary formed by the ion concerned can be followed.

Equivalent-conductance Method.   If 1 gram-equivalent of a cation is placed between electrodes 1 cm. apart, the amperage (coulombs per second) of the current carried by that ion will be $96,500 U_c$, if the velocity, U_c, of the cation is expressed in centimeters per second.   If the potential drop between the electrodes is 1 volt, Eq. (6-9) indicates that the amperage due to the cation is numerically equal to the equivalent conductance of the cation. Under the stated conditions the velocity of the ion is equal to its mobility.   Therefore, we can establish the relation between equivalent conductance and mobility

$$\text{Mobility of cation} = \frac{\lambda_c}{96,500}$$

and similarly for the anion

$$\text{Mobility of anion} = \frac{\lambda_a}{96,500}$$

Just as equivalent conductances increase with decreasing concentration, so will mobilities increase to a maximum at infinite dilution.

Table 6-7 also shows the mobilities at infinite dilution for some ions.

The Ionization of Water.   Water is a conductor of electricity, although an extremely poor one.   It is to be classed as a very weak electrolyte, ionizing as follows:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
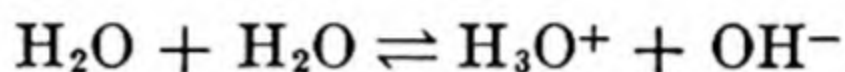
Water is thus to be classified as both an acid and a base, since it can serve as both a proton donor and proton acceptor.

The degree of ionization of water can be calculated as follows: The specific conductance of pure water, at 25°C., is 5.44×10^{-8} mho.   The volume of 1 gram-equivalent (18.0 g.) of water, at 25°C., is 18.1 ml.   Therefore, the equivalent conductance of water is

$$5.44 \times 10^{-8} \times 18.1 = 9.90 \times 10^{-7} \text{ mho}$$

The equivalent conductance of water at infinite dilution is equal to the sum of the equivalent conductances at infinite dilution of hydronium and hydroxide ion.   Using the values in Table 6-7, we find

$$H_2O, \Lambda_\infty = 349.8 + 197.6 = 547.4 \text{ mhos}$$

Therefore, using Eq. (6-15), we find the degree of ionization of water, at 25°C., to be

$$\frac{\Lambda}{\Lambda_\infty} = \frac{9.90 \times 10^{-7}}{547.4} = 1.81 \times 10^{-9}$$

Amphoteric Electrolytes.   In addition to water there are other substances that are capable of acting as both proton donors and proton acceptors, *i.e.*, as both acids and bases.   Substances that behave in this way are known as *amphoteric electrolytes*.   This name is usually condensed to *ampholyte*.[1]   The ampholytes most commonly encountered in physiological work are organic compounds, such as the amino acids and proteins.   Amino acetic

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[1] The term *amphiprotic* is also used to describe these substances, indicating their ability both to donate and to accept protons.

acid, or glycine, may be used as an example to illustrate their behavior. The formula for acetic acid may be written as CH_3COOH. If an amino group (NH_2) is substituted for one of the hydrogen atoms on the methyl group, acetic acid is converted to glycine,

$$NH_2CH_2COOH$$
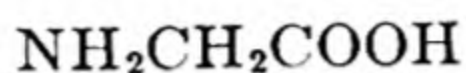
For reasons that will be discussed in the next chapter, it is believed that practically all the glycine in solution is present as

$$^+NH_3CH_2COO^-$$

This form results from the transfer of a proton from the carboxyl group to the amino group. The doubly charged ion so produced is known as a *zwitterion* or *amphion* or *dipolar ion*. It has a high dipole moment and the dielectric constant of its aqueous solutions is much larger than that of water. This amphion can serve either as an acid, giving up a proton from the $^+NH_3$ group, or as a base, accepting a proton on the COO^- group.

Effects of Ions on the Human Body. As will be shown later, one of the substances useful in maintaining a constant concentration of hydronium ion in the blood is the bicarbonate ion. Various ions also have a striking effect on the action of the heart. Any salt solution used for injection into the blood must be isotonic with that fluid. Isotonicity, however, is not sufficient. If a heart is bathed with a sodium chloride solution of correct tone, the heart nevertheless soon ceases to beat because of the toxic effect of the sodium ions. This effect can be counteracted by the addition of calcium ions, but the latter in turn produce too great a state of muscular contraction in the heart. This effect of the calcium ions can be neutralized by the addition of potassium ions. Therefore, a solution to be injected into the blood stream must have not only the same tone as does blood, but must also contain the three ions, sodium, potassium, and calcium, in definite proportions. It is for this reason that Locke's physiological salt solution has the composition indicated in Table 5-4.

Many other ions are of importance physiologically. For example, magnesium, iron, copper, manganese, zinc, phosphate, bromide, and iodide ions are all essential to the normal functioning of the body.

Problems

1. The freezing point of $0.050m$ sodium sulfate in water is $-0.223°C$. What is the value of the van't Hoff factor for this solution?

2. Calculate the freezing point of $0.01m$ barium chloride in water.

3. How many coulombs of electricity is carried by 10 g. of each of the following ions: hydronium, calcium, aluminum, hydroxide, sulfate?

4. How many grams of cation will be discharged by the passage of 10,000 coulombs through each of the following solutions: hydrochloric acid, cupric sulfate, nickel chloride?

5. What is the normality of each of the following solutions: $0.03M$ hydrochloric acid, $1.6M$ sulfuric acid, $0.045M$ ferric sulfate?

6. What is the molarity of each of the following solutions: $6.0N$ nitric acid, $2.7N$ barium chloride, $0.001N$ phosphoric acid, $0.024N$ aluminum sulfate?

7. How many grams of solute is present in 175 ml. of $0.15N$ calcium chloride solution?

8. If 37 ml. of $0.05M$ sodium hydroxide is neutralized by 23 ml. of sulfuric acid, what is the molarity of the acid?

9. A solution of silver nitrate contains 80.00 g. of the solute per liter. How many milliliters of this solution is required to precipitate the chloride ion in 25 ml. of $0.17M$ barium chloride solution?

10. Given a stock solution of phosphoric acid that is 1.60 molar, how should you proceed to prepare 700 ml. of a 2.00 normal solution of the acid?

11. What reasonable explanation can you give for the fact that electrovalent compounds in general have higher melting points and higher boiling points than covalent compounds have?

12. A solution contains 0.001 mole of sodium sulfate and 0.001 mole of potassium chloride per liter. Calculate the ionic strength of the solution and the activity of each ion.

13. A 0.01 normal solution of potassium chloride is placed between electrodes that are 10 cm.^{2} in area and are 3 cm. apart. If the potential drop between the electrodes is 5 volts, calculate the amperage of the current that flows through the solution. Temperature is 25°C.

14. From the data in Table 6-6, calculate the degree of ionization of $0.01M$ acetic acid. Also calculate the value of the van't Hoff factor for the same solution.

15. From the following data and from that given in Tables 6-5 and 6-7, calculate the degree of ionization of $0.1N$ ammonium hydroxide. The apparatus used is illustrated in Fig. 6-5. When the cell H contains $0.1N$ ammonium hydroxide and when the resistance in R is 1,000 ohms, the silent point occurs when AD equals 653 mm. and DB equals 347 mm. Using the same cell, $0.1N$ potassium chloride was found to have an observed conductance of 0.0178 mho. Temperature is 25°C.

16. What are the values of the transference numbers, at infinite dilution, of the ions in the following electrolytes: sulfuric acid, potassium nitrate, sodium hydroxide, magnesium chloride?

CHAPTER 7

CHEMICAL EQUILIBRIUM

In the preceding chapters, various examples of change of physical state have been cited, such as the change of water from a liquid to a vapor, or the change of sugar from the solid to the dissolved state. It was shown that these changes were reversible and so might be written

$$H_2O \text{ (liquid)} \rightleftharpoons H_2O \text{ (vapor)}$$
$$C_{12}H_{22}O_{11} \text{ (solid)} \rightleftharpoons C_{12}H_{22}O_{11} \text{ (dissolved)}$$
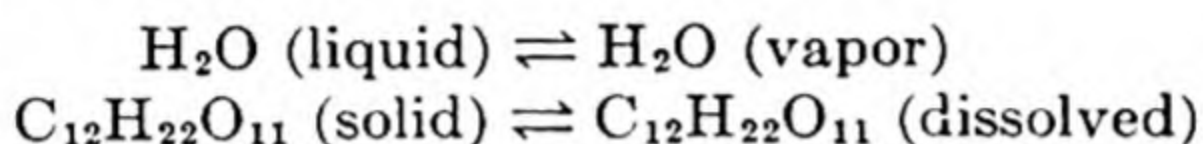
In these reversible physical changes a condition of equilibrium is attainable, at which point the speeds of the forward and reverse reactions are equal, and no apparent further change takes place.

Chemical changes are likewise reversible to a greater or lesser degree. Therefore, it should be possible, in a chemical change, to reach a state of equilibrium, and the criterion of this state is the same as that for equilibrium in a physical change, *viz.*, that the speed of the forward and the reverse reactions shall be the same.

EQUILIBRIUM IN REACTIONS BETWEEN MOLECULES

Consider a chemical reaction in which one molecule of A reacts with one molecule of B to produce one molecule of C and one molecule of D. Consider further that this reaction is reversible; *i.e.*, one molecule each of C and D will react to form one molecule each of A and B. This reaction can be written

$$A + B \rightleftharpoons C + D$$
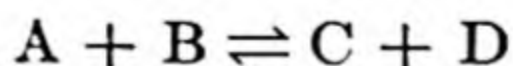
When equilibrium is reached, the forward speed is equal to the speed in the reverse direction. These speeds in a chemical reaction are defined as the *number of moles of substance transformed per unit volume in unit time.* The unit of volume is usually the liter.

Factors Affecting the Speed of a Reaction. The speed of any chemical reaction is determined by five factors:

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1. The chemical affinity of the reacting substances.
2. The temperature.
3. The presence or absence of solvents.
4. The presence or absence of catalytic agents.
5. The concentration of the reacting substances.

Of these five factors the most important for the present discussion is the last. In studying the effect of concentration on the speed of reaction, the practice is to hold the first four factors constant and to measure the speed at varied concentrations of the reactants. When this is done, it is found that the *speed of the reaction is proportional to the product of the concentrations of*
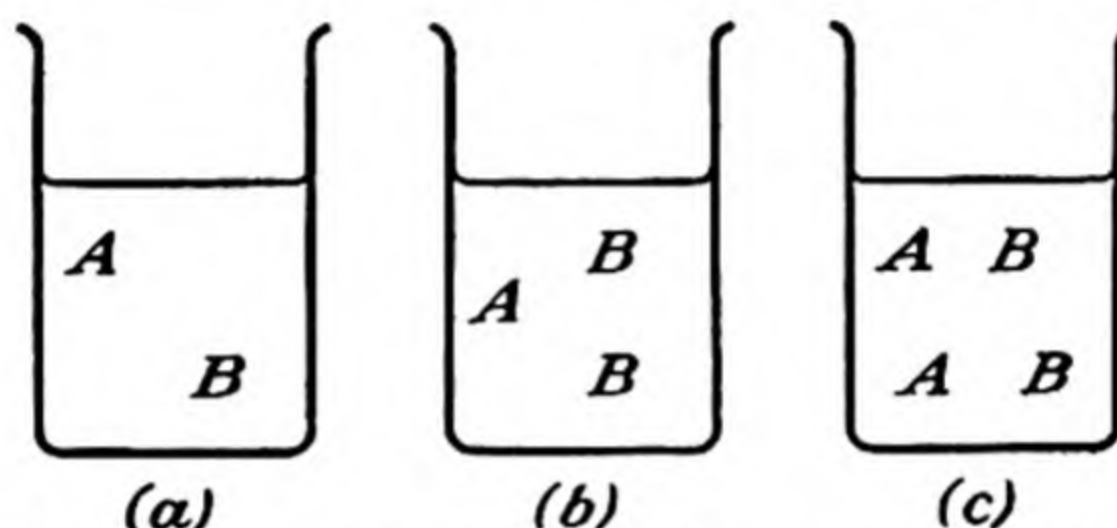
FIG. 7-1. The relation between speed of reaction and concentration of reactants.

the reacting substances. This statement is known as the *law of mass action.* That this conclusion is a reasonable one may be seen from the following example. In Fig. 7-1 the forward reaction $A + B \rightarrow C + D$ is represented as taking place, in each case, in 1 liter of solution. In (*a*) this liter of solution contains one molecule of A and one molecule of B. In order for A and B to react, they must come in contact with each other.[1] Therefore, the speed of the reaction is determined by the probability that A will hit B in the course of their random motion through the solution. Let us say arbitrarily that this probability is 1 in (*a*). In (*b*) it is apparent that the chance of A hitting a molecule of B

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[1] It does not necessarily follow that every contact between A and B will result in the production of C and D. The molecules must possess, at the moment of contact, a certain minimum energy in order for the reaction to take place. Only a very small fraction of the molecules will possess this required energy. Therefore, only a very small fraction of the contacts will be fruitful. As the temperature of the system is raised, not only will the speed of the molecules and, therefore, the number of contacts be increased, but also a greater proportion of the molecules will possess the necessary energy. Consequently, a greater fraction of the contacts will be productive. Both of these factors will increase the speed of the reaction.

is twice as great as in (a); in other words, the probability is 2, and the reaction will proceed twice as fast. Likewise in (c) the chance of a molecule of A hitting one of B is twice as great as it was in (b), or the probability is 4 and the speed of the reaction is four times as great as it is in (a). It will be noted that these speeds are proportional to the product of the concentrations of A and B.

The dependence of the speed of a reaction upon the concentration of the reacting substances may be demonstrated by the following experiment. If dilute sulfurous acid is added to an excess of dilute iodic acid, the following reaction takes place:

$$HIO_3 + 3H_2SO_3 \rightarrow HI + 3H_2SO_4$$
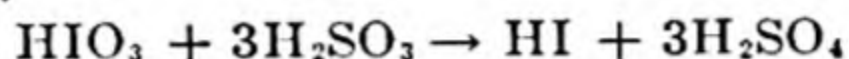
The hydriodic acid thus formed will react with the excess iodic acid as follows:

$$HIO_3 + 5HI \rightarrow 3H_2O + 3I_2$$
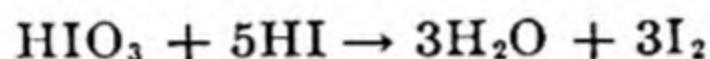
The iodine formed will turn starch solution blue. The first reaction is slow and must go practically to completion before the second reaction will proceed to any detectable extent. The second reaction is practically instantaneous. Therefore, the length of time before the blue color appears is a measure of the speed of the first reaction.

Prepare the following stock solutions: 0.5M iodic acid, 0.5M sulfurous acid, and starch solution. The starch solution may be prepared by mixing 1 g. of potato starch with a little cold water and pouring the resulting paste into 1 liter of boiling water.

In a 100-ml. graduate, put 2 ml. of the iodic acid, 10 ml. of the starch solution, and enough water to make a total volume of 100 ml. In a second graduate, put 2 ml. of sulfurous acid and enough water to make the total volume 100 ml. Pour the contents of the two graduates into a flask, mix them thoroughly, and note the length of time it takes the blue color to appear.

Repeat the experiment using 1 ml. of iodic acid and 1 ml. of sulfurous acid, but keeping the amount of starch and the total volume of each solution the same as before. Note that it takes longer for the blue color to appear than it did in the first case.

In the reaction $A + B \rightleftharpoons C + D$, if the first four factors affecting the speed of the reaction are held constant and if their effect on the forward speed of the reaction is expressed by the constant k_1, then it can be said that the forward speed is equal to $k_1[A][B]$. If the effect of these factors on the speed in the reverse direction is expressed by the constant k_2, then the reverse speed is equal to $k_2[C][D]$. Whenever the formula for a substance appears in square brackets, the expression stands for the concentration of that substance in moles per liter.

We have seen that at equilibrium the forward speed is equal to the reverse speed. From this it follows that, also at equilibrium,

$$k_1[A][B] = k_2[C][D]$$

or

$$\frac{k_1}{k_2} = \frac{[C][D]}{[A][B]} = K_{eq} \tag{7-1}$$

The expression K_{eq} is known as the *equilibrium constant* for the reaction in question. The convention followed in this text is that the equilibrium constant is equal to the product of the concentrations of the substances appearing on the right-hand side of the reaction, as written, divided by the product of the concentrations of the substances appearing on the left-hand side.

Stated in words, Eq. (7-1) says that, in any given chemical reaction at equilibrium, the value of the product of the concentrations of those substances on the right-hand side of the reaction divided by the product of the concentrations of those on the left-hand side is a constant, if the temperature is constant. It is not necessary that the relative amounts of the reacting substances present be the same as that expressed in the chemical equation for the reaction. The sole criterion of equilibrium is that the ratio of the products of their concentrations shall be equal to the equilibrium constant.

Changes in the concentration of the reacting substances have little effect on the value of the equilibrium constant. Changes in temperature, however, have different effects on the values of k_1 and k_2 and hence will change the value of their ratio, the equilibrium constant. Methods for determining the individual values of k_1 and k_2 will be discussed in Chap. 11. For the present discussion, these individual values are not necessary, only the value of their ratio.

Example. In the reaction between ethyl alcohol and acetic acid to produce ethyl acetate and water, it is found that the following concentrations are present at equilibrium:

$$C_2H_5OH + HCH_3CO_2 \rightleftharpoons C_2H_5CH_3CO_2 + H_2O$$
$$0.1 0.1 0.2 0.2$$
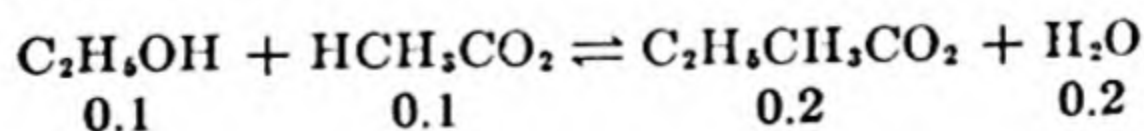
Substituting these values in Eq. (7-1) gives

$$K_{eq} = \frac{[C_2H_5CH_3CO_2][H_2O]}{[C_2H_5OH][HCH_3CO_2]} = \frac{0.2 \times 0.2}{0.1 \times 0.1} = 4.0$$

Therefore, In any mixture of these four substances, if equilibrium is established, the ratio of the products of their concentrations must always be equal to 4.0. Any set of values that satisfies this requirement represents equilibrium conditions. For example, each of the following mixtures is at equilibrium:

$$C_2H_5OH + HCH_3CO_2 \rightleftharpoons C_2H_5CH_3CO_2 + H_2O$$

1.0	1.0	1.0	4.0
1.5	2.0	6.0	2.0
0.4	0.5	0.8	1.0
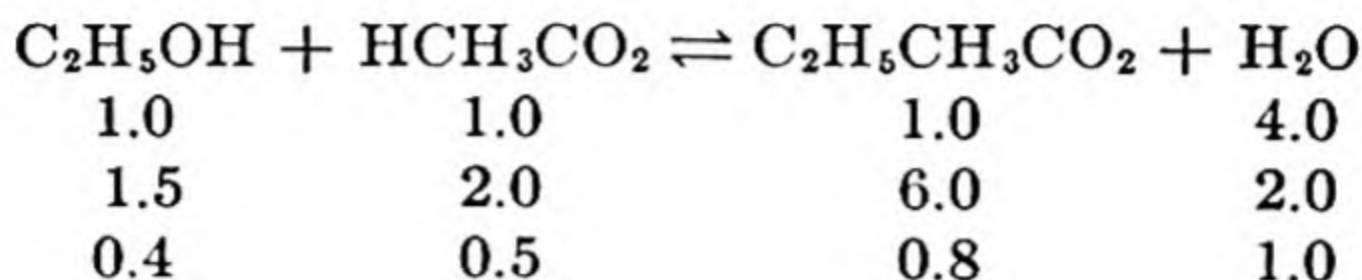
If the system is not in equilibrium, it is possible to predict which way the reaction will go and how far it will go, if the value of the equilibrium constant is known.

Example. If a system contains 1 mole of ethyl alcohol, 2 moles of acetic acid, 3 moles of ethyl acetate, and 4 moles of water, in which direction will the reaction go and how far will it proceed? Substituting these values in the expression for the equilibrium constant of the reaction gives

$$\frac{[C_2H_5CH_3CO_2][H_2O]}{[C_2H_5OH][HCH_3CO_2]} = \frac{3 \times 4}{1 \times 2} = 6.0$$

This value is greater than that of the equilibrium constant for the reaction. Therefore, in order to reach equilibrium, the numerator must be decreased and the denominator increased until the value of the fraction is equal to 4.0. This means that ethyl acetate and water will be used up while ethyl alcohol and acetic acid will be formed. Let x represent the number of moles of water used up. Then, since one molecule of each substance is involved in the reaction, the conditions at equilibrium will be represented as

$$C_2H_5OH + HCH_3CO_2 \rightleftharpoons C_2H_5CH_3CO_2 + H_2O$$
$$(1 + x) \qquad (2 + x) \qquad (3 - x) \qquad (4 - x)$$
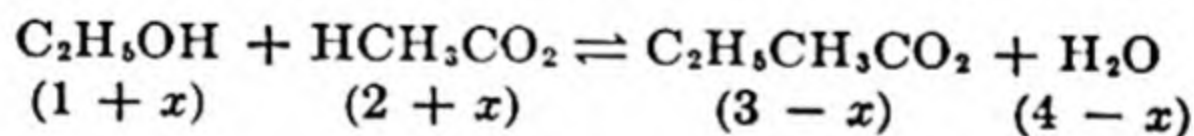
and these values must satisfy the expression

$$\frac{(3 - x)(4 - x)}{(1 + x)(2 + x)} = 4.0$$

Upon solving this expression we find that x equals -6.5, or $+0.20$. The negative value is obviously not applicable. Therefore, the moles of each substance present at equilibrium are

$$C_2H_5OH + HCH_3CO_2 \rightleftharpoons C_2H_5CH_3CO_2 + H_2O$$

| 1.2 | 2.2 | 2.8 | 3.8 |
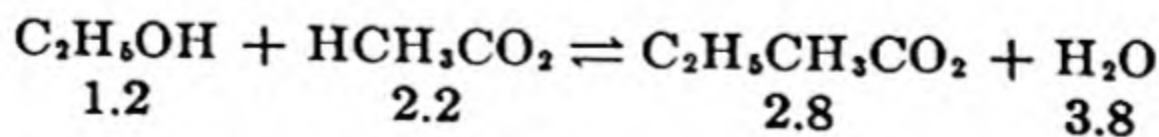
If a reaction involves more than one of each kind of molecule, the expression for the equilibrium constant becomes more complicated. Consider the reaction $A + 2B \rightleftharpoons C + D$, and

let us see how the value of the equilibrium constant is related to the concentrations of A, B, C, and D.   This reaction may be considered as taking place in two steps:

$$(1) \quad A + B \rightleftharpoons AB$$
$$(2) \quad AB + B \rightleftharpoons C + D$$
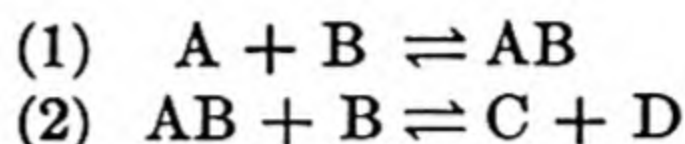
The equilibrium constant for reaction (1) is given by the expression

$$K'_{eq} = \frac{[AB]}{[A][B]} \tag{7-2}$$

from which we find that $[AB] = K'_{eq}[A][B]$.

The equilibrium constant for reaction (2) is given by the expression

$$K''_{eq} = \frac{[C][D]}{[AB][B]} \tag{7-3}$$

Since reactions (1) and (2) are taking place in the same vessel, the expression [B] occurring in Eqs. (7-2) and (7-3) represents in each case the total concentration of B present, because all the B molecules are available for each reaction.   This idea seems to be one of the most difficult to grasp in the whole discussion of equilibrium.   It appears at first that if some B is used up in reaction (1) there must necessarily be less of it available to take part in reaction (2).   But it must be remembered that both reactions are reversible and are at equilibrium, which means that as fast as a molecule of B is used up by the forward reaction in one part of the solution another molecule of B is released by the reverse reaction in another part.   Therefore, the concentration of B at equilibrium remains constant.

Substituting in Eq. (7-3) the value of [AB] obtained from Eq. (7-2) gives

$$K''_{eq} = \frac{[C][D]}{K'_{eq}[A][B][B]} \tag{7-4}$$

The equilibrium constant for the whole reaction will be given by the following expression:

$$K_{eq} = K'_{eq} K''_{eq} = \frac{[C][D]}{[A][B]^2} \tag{7-5}$$

In other words, the number of molecules of a substance appearing in the balanced equation for the reaction appears as an exponent

for the concentration of that substance in the expression for the equilibrium constant. In general, for the reaction

$$m\text{A} + n\text{B} \rightleftharpoons p\text{C} + q\text{D}$$
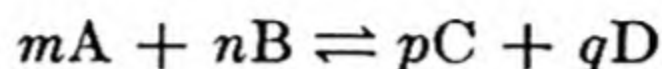
the expression for the equilibrium constant is

$$K_{eq} = \frac{[\text{C}]^p[\text{D}]^q}{[\text{A}]^m[\text{B}]^n} \tag{7-6}$$

For equilibriums in which gases are involved, it is customary to substitute the partial pressure of the gas for its concentration. This is possible since the concentration of a gas is directly proportional to its partial pressure. For example, the equilibrium constant for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ can be written

$$K_{eq} = \frac{p_{NH_3}^2}{p_{N_2} \times p_{H_2}^3}$$

RELATION BETWEEN pH AND CONCENTRATION OF HYDRONIUM ION

Since, in all the different types of equilibrium in protolytic reactions, we shall be interested in the resulting concentration of hydronium ion in the solution, it will be well, before considering these equilibriums, to become familiar with an alternative method for expressing the concentration of hydronium ion, *viz.*, the pH of a solution.

Concentration of hydronium ion can be expressed in terms of moles per liter. For many purposes this method of expression is satisfactory. It does, however, possess certain disadvantages. It is frequently desirable to show graphically the changes in hydronium-ion concentration in a solution as the solution changes from strongly acidic to strongly basic. Such a change might well involve a variation in the hydronium-ion concentration over a range from 1.0 mole/liter to 0.000,000,000,000,01 mole/liter. In this range the change of hydronium-ion concentration from 0.000,000,000,000,02 mole/liter to 0.000,000,000,000,01 mole/ liter is just as significant as the change from 1.0 mole/liter to 0.5 mole/liter. The same amount of sodium hydroxide must be added per liter of solution to produce either of the two changes. A scale that was large enough to show the first change would have to extend to an impractical size to include the second. Further-

more, the ratio of the lengths of the lines showing the two changes would be out of all proportion to their relative significance, which is actually about the same.

To overcome this disadvantage, the Danish chemist Sørensen suggested that the concentration of hydrogen ion (as the hydronium ion was called at that time) be expressed not in moles per liter, but in terms of the negative value of the power to which 10 must be raised to equal numerically the concentration of hydrogen ion in moles per liter. This power of the hydrogen-ion concentration is indicated by the symbol pH. This new unit is commonly defined by the expression

$$pH = \log \frac{1}{[H_3O^+]} = -\log [H_3O^+]$$

Using this pH unit it is possible, on a graph of reasonable dimensions, to show the changes of hydronium-ion concentration over a wide range. Furthermore, the lengths of the various segments of the curve give an idea of the relative significance of the changes in the hydronium-ion concentration. For example, the change from 1.0 mole/liter to 0.5 mole/liter corresponds to a change in pH from 0.0 to 0.3, and the change from 0.000,000,000,000,02 mole/liter to 0.000,000,000,000,01 mole/liter corresponds to a change in pH from 13.7 to 14.0, indicating that the two changes are of equal importance.

It thus appears that the pH scale serves a useful purpose and was not designed simply to harass the student. An ability to convert the concentration of hydronium ion in moles per liter into pH, and vice versa, will well repay the time and effort spent in acquiring it.

Conversion of Moles per Liter into pH. As the first step in this conversion, the number expressing the concentration of hydronium ion in moles per liter should be written so that it consists of some number between 1 and 10, multiplied by 10 raised to some integral power. For example,

$$0.0200 = 2.00 \times 10^{-2}$$
$$0.0057 = 5.7 \times 10^{-3}$$

Next, the logarithms of these numbers are obtained, remembering that the logarithm of a product is equal to the sum of the logarithms of its factors.

$$\log 2.00 \times 10^{-2} = \log 2.00 + \log 10^{-2} = 0.30 + (-2.00)$$
$$= -1.70$$
$$\log 5.7 \ \times 10^{-3} = \log 5.7 \ + \log 10^{-3} = 0.76 + (-3.00)$$
$$= -2.24$$

The pH in each case is the negative value of the logarithm.

$[H_3O^+]$	pH
0.0200	1.70
0.0057	2.24

Conversion of pH into Moles per Liter. This conversion seems to present greater obstacles to the student than does the preceding one. Actually it should be just as simple when the various intermediate steps are understood. Let us consider in detail a typical example.

If the pH of a solution is 6.75, what is the concentration of hydronium ion in the solution in moles per liter?

Since $pH = - \log [H_3O^+]$, it follows that, in this case, $\log [H_3O^+] = -6.75$. This number is a logarithm consisting of two parts: a characteristic (that part lying to the left of the decimal point) and a mantissa (that part lying to the right of the decimal point). The minus sign in front means that the whole logarithm, both characteristic and mantissa, is negative. Now, while it would be possible to write a logarithm table containing negative mantissas, the ones in common use contain only positive mantissas. Therefore, in order to look up the antilogarithm of -6.75 in the ordinary logarithm table, it will be necessary to convert -6.75 to an equivalent number having a positive mantissa. This may be done by making the characteristic 1 greater negatively and subtracting the mantissa from 1.0. Treated in this way, -6.75 becomes $\bar{7}.25$. The minus sign over the characteristic indicates that it alone is negative; the mantissa is positive. These two numbers are equal to each other

$$-6.75 = \bar{7}.25$$

and the latter has a positive mantissa whose antilogarithm can be looked up in the ordinary logarithm table.

$$\text{antilog } 0.25 = 1.78$$

If we now multiply by 10 raised to the power corresponding to the characteristic of the logarithm, we shall have the correct answer: 1.78×10^{-7}.

pH	$[H_3O^+]$
6.75	1.78×10^{-7}

A relationship similar to that between pH and the concentration of hydronium ion has been used for other ions as well.

$$pOH = - \log [OH^-]$$

This relationship has also been extended to equilibrium constants.

$$pK = - \log K$$

For example, we shall see that for acetic acid the value of $K_a = 1.8 \times 10^{-5}$. The corresponding value of $pK_a = 4.74$.

Equilibrium in Protolytic Reactions

Under this topic we shall limit our consideration to proton exchanges which occur in dilute aqueous solution. We shall further restrict it to those acids which are sufficiently weak as proton donors so that an equilibrium constant for their reaction with water can be established, and to those bases which are sufficiently weak as proton acceptors so that an equilibrium constant for their reaction with water can likewise be established.

For example, hydrogen chloride is so strong a proton donor that in dilute aqueous solution it gives up its protons almost completely to water and no equilibrium constant for the reaction can be established. The same is true of nitric and perchloric acids, and the first proton of sulfuric acid. There are means for estimating the relative strengths of these acids as proton donors, but that is outside the scope of the present discussion.[1]

All the protolytic equilibriums in which we are interested fall into one of the following five classes:

1. Equilibrium in pure water.
2. Equilibrium in aqueous solutions of weak acids.
3. Equilibrium in aqueous solutions of weak bases.
4. Equilibrium in aqueous solutions containing a weak acid and its conjugate weak base.

[1] HAMMETT, L. P., and A. J. DEYRUP, *J. Am. Chem. Soc.*, **54**, 2721 (1932).

5. Equilibrium in aqueous solutions containing equivalent quantities of a weak acid and a weak base which is not conjugate to it.

1. *Equilibrium in Pure Water*

Water molecules can act as both proton donors and proton acceptors according to the reaction
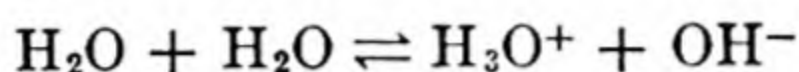
$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

for which the equilibrium constant has the form

$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]}$$

Since, at 25°C., the concentration of pure water is a constant value, equal approximately to 55.4 moles/liter, the expression for the equilibrium constant can be rearranged to read

$$K_w = (55.4)^2 K_{eq} = [H_3O^+][OH^-]$$

where K_w is known as the ion-product constant for water.

In Chap. 6 the degree of ionization of water was found to be 1.81×10^{-9}, at 25°C. From this we can calculate the concentration of hydronium and of hydroxide ions in pure water, at 25°C., to be

$$1.81 \times 10^{-9} \times 55.4 = 1.00 \times 10^{-7} \text{ mole/liter}$$

From this it follows that, at 25°C.,

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \qquad (7\text{-}7)$$

or

$$pK_w = pH + pOH = 14.00 \qquad (7\text{-}8)$$

The value of K_w increases slightly with rising temperature.

This relationship holds not only in pure water but, sufficiently well for our purposes, in dilute aqueous solutions. Stated in words, it means that in pure water, or in any dilute aqueous solution, the product of the concentrations of the hydronium and hydroxide ions is a constant value, equal to 1.00×10^{-14}. This means that, if the concentration of either one of these ions in an aqueous solution is known, the concentration of the other can be calculated. In pure water the concentration of hydronium ion is 1.00×10^{-7} mole/liter. Any solution in which the concentra-

tion of hydronium ion is more than this amount is acid; one in which the concentration of hydronium ion is less than 1.00×10^{-7} mole/liter is basic. The relationship between concentration of hydronium ion and concentration of hydroxide ion and the relationship between pH and pOH is shown in Table 7-1.

TABLE 7-1. VALUES OF THE CONCENTRATION OF HYDRONIUM ION AND pH AND THE CORRESPONDING VALUES OF CONCENTRATION OF HYDROXIDE ION AND pOH

Solution	$[H_3O^+]$	$[OH^-]$	pH	pOH
Acid.....................	1.00×10^{-4}	1.00×10^{-10}	4.00	10.00
	1.00×10^{-5}	1.00×10^{-9}	5.00	9.00
	1.00×10^{-6}	1.00×10^{-8}	6.00	8.00
Neutral...............	1.00×10^{-7}	1.00×10^{-7}	7.00	7.00
	1.00×10^{-8}	1.00×10^{-6}	8.00	6.00
Basic................	1.00×10^{-9}	1.00×10^{-5}	9.00	5.00
	1.00×10^{-10}	1.00×10^{-4}	10.00	4.00

Example 1. What is the concentration of hydroxide ion in an acid solution in which the concentration of hydronium ion is 0.0150 mole/liter?

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.00 \times 10^{-14}}{1.50 \times 10^{-2}} = 6.67 \times 10^{-13}$$

Example 2. What is the pH of a solution of ammonia whose pOH is 3.40?

$$pH = pK_w - pOH = 14.00 - 3.40 = 10.60$$

2. *Equilibrium in Aqueous Solutions of Weak Acids*

A. Monoprotic Acids. Monoprotic acids are ones which give off one proton per unit. The unit may be a neutral molecule (HCH_3CO_2), a cation (NH_4^+), or an anion (HCO_3^-).

Hydronium ion is the strongest acid that can exist in significant concentration in dilute aqueous solution. All stronger acids give up their protons practically completely to water when in dilute solution in it. In Table 7-2 are listed some typical acids, all of them weak except hydronium ion. Their strength as proton donors decreases from top to bottom of the list. Water is not the weakest acid known, for example ethyl alcohol is weaker, but the list is sufficient for our purposes.

In developing the expressions for the constants for a weak monoprotic acid we shall use HA as the general formula for such

an acid. Its reaction with water may be represented as

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
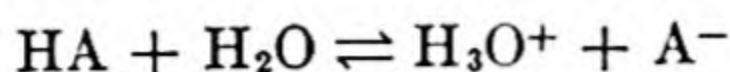
For this reversible reaction the equilibrium constant has the form

$$K_{eq} = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

Since, in dilute aqueous solutions at 25°C. the concentration of water is practically a constant at 55.4 moles/liter, we may rewrite this expression to read

$$K_a = 55.4K_{eq} = \frac{[H_3O^+][A^-]}{[HA]} \qquad (7\text{-}9)$$

in which K_a is the protolysis constant for the reaction.

TABLE 7-2. VALUES OF THE PROTOLYSIS CONSTANTS IN AQUEOUS SOLUTION FOR SOME WEAK ACIDS AND WEAK BASES, AND THE CORRESPONDING pK VALUES, AT 25°C.*

pK_a	K_a	Acid-conjugate-base		K_b	pK_b
$-\ 1.74$	55.4	H_3O^+	H_2O	1.8×10^{-16}	$+15.74$
$+\ 2.12$	7.6×10^{-3}	H_3PO_4	$H_2PO_4{}^-$	1.3×10^{-12}	$+11.88$
$+\ 3.74$	1.8×10^{-4}	$HCOOH$	$COOH^-$	5.6×10^{-11}	$+10.26$
$+\ 4.62$	2.4×10^{-5}	$C_6H_5NH_3{}^+$	$C_6H_5NH_2$	4.1×10^{-10}	$+\ 9.38$
$+\ 4.74$	1.8×10^{-5}	HCH_3CO_2	$CH_3CO_2{}^-$	5.6×10^{-10}	$+\ 9.26$
$+\ 6.37$	4.3×10^{-7}	H_2CO_3	$HCO_3{}^-$	2.3×10^{-8}	$+\ 7.63$
$+\ 7.21$	6.2×10^{-8}	$H_2PO_4{}^-$	$HPO_4{}^{--}$	1.6×10^{-7}	$+\ 6.79$
$+\ 9.14$	7.2×10^{-10}	HCN	CN^-	1.4×10^{-5}	$+\ 4.86$
$+\ 9.26$	5.6×10^{-10}	$NH_4{}^+$	NH_3	1.8×10^{-5}	$+\ 4.74$
$+10.33$	4.7×10^{-11}	$HCO_3{}^-$	$CO_3{}^{--}$	2.1×10^{-4}	$+\ 3.67$
$+12.3$	$5\ \ \times 10^{-13}$	$HPO_4{}^{--}$	$PO_4{}^{---}$	$2\ \ \times 10^{-2}$	$+\ 1.7$
$+15.74$	1.8×10^{-16}	H_2O	OH^-	55.4	$-\ 1.74$

* It should be noted that these values for the protolysis constants apply only to aqueous solutions of the acids and bases. When they are dissolved in a solvent whose proton donating and accepting abilities differ from those of water the values of the protolysis constants may be quite different from those given here. Even the order in which they occur may be changed.

Values of the protolysis constants and the corresponding pK_a values are given for the acids listed in Table 7-2. It will be noted that the weaker the acid, the smaller is the value of K_a and the larger is the value of pK_a.

The value of the protolysis constant for the hydronium ion

may be arrived at by considering it as a typical acid, for which the reaction with water is
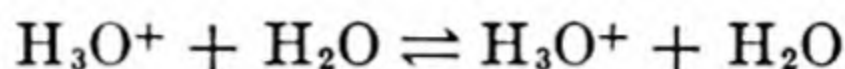
$$H_3O^+ + H_2O \rightleftharpoons H_3O^+ + H_2O$$

For this reaction the equilibrium constant has the form

$$K_{eq} = \frac{[H_3O^+][H_2O]}{[H_3O^+][H_2O]}$$

and from this we may, as in the preceding case, get the expression for the protolysis constant

$$K_a = 55.4K_{eq} = \frac{[H_3O^+][H_2O]}{[H_3O^+]} = [H_2O] = 55.4$$

This gives an idea of the strength of the hydronium ion as a proton donor compared to the weak acids listed.

In order to compare water, as a proton donor, with other weak acids we may derive its protolysis constant as follows:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]}$$
$$K_a = 55.4K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O]} = \frac{1.00 \times 10^{-14}}{55.4} = 1.8 \times 10^{-16}$$

The Ostwald Dilution Law. A different expression for the protolysis constant for a weak acid can be derived as follows. Let c represent the original concentration of the acid; let α represent the *degree of protolysis, i.e.,* the fraction of the original amount of acid that has been converted into the conjugate base. Then, at equilibrium, the concentrations of the various components of the solution will be

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
$$(1 - \alpha)c \qquad \alpha c \qquad \alpha c$$
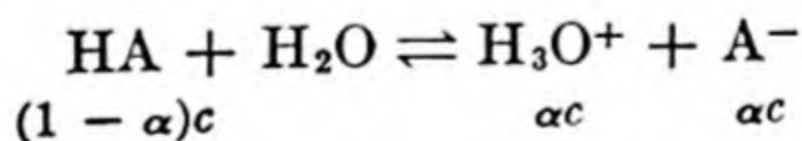
Substitution of these expressions for the concentrations in Eq. (7-9) gives

$$K_a = \frac{\alpha^2 c}{1 - \alpha} \qquad (7\text{-}10)$$

This expression is known as the *Ostwald dilution law.*

Supposedly the only factor that will change the value of the

protolysis constant for a given reaction is a change in temperature. For dilute solutions the value of the protolysis constant should be independent of the concentration; as the concentration changes the degree of protolysis also changes in such a way as to maintain a constant value for the protolysis constant. While this is approximately true, actually, the value of the protolysis constant increases slightly with increase in the ionic strength of the solution. This is illustrated in Table 7-3. The reason for this change will be discussed in the section on the "salt effect."

Example. At 25°C., the degree of protolysis of acetic acid in 0.0200 molar solution is 2.99 per cent. Calculate the value of the protolysis constant for acetic acid. Use Eq. (7-10) and substitute the following values: $\alpha = 0.0299$, $c = 0.0200$.

$$K_a = \frac{(0.0299)^2 \times 0.0200}{(1 - 0.0299)} = 1.84 \times 10^{-5}$$

TABLE 7-3. VALUES OF THE PROTOLYSIS CONSTANT FOR ACETIC ACID, AT 25°C.

c	α	K_a
0.2000	0.0095	1.821×10^{-5}
0.1000	0.0135	1.846×10^{-5}
0.0500	0.0190	1.849×10^{-5}
0.0200	0.0299	1.840×10^{-5}
0.0098	0.0422	1.832×10^{-5}
0.0059	0.0540	1.823×10^{-5}
0.0010	0.1238	1.797×10^{-5}

Once the value of the protolysis constant for a weak acid has been determined, it is possible, by use of Eq. (7-10), to determine the degree of protolysis of that acid at any concentration within the range in which the value of K_a is approximately constant. The calculation can be simplified by taking advantage of the fact that, if K_a is of the order of 10^{-4} or less, then the value of α is so small that the error introduced by assuming, in Eq. (7-10), that $(1 - \alpha) = 1.0$, can be neglected.

Equation (7-10) would then read $K_a = \alpha^2 c$ and could be solved for the degree of protolysis to give

$$\alpha = \sqrt{\frac{K_a}{c}} \qquad (7-11)$$

We have seen previously that, in a solution of a weak acid, the concentration of hydronium ion is equal to αc. Combining this with Eq. (7-11) we find

$$[H_3O^+] = c\sqrt{\frac{K_a}{c}} = \sqrt{\frac{K_a c^2}{c}} = \sqrt{K_a c} \qquad (7\text{-}12)$$

or

$$pH = \tfrac{1}{2}(pK_a - \log c) \qquad (7\text{-}13)$$

Example. Calculate the degree of protolysis and the concentration of hydronium ion in $0.0050M$ acetic acid.

$$\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{5.0 \times 10^{-3}}} = \sqrt{36 \times 10^{-4}} = 6 \times 10^{-2}$$

$$[H_3O^+] = \sqrt{1.8 \times 10^{-5} \times 5.0 \times 10^{-3}} = \sqrt{9.0 \times 10^{-8}} = 3.0 \times 10^{-4}$$

$$pH = \tfrac{1}{2}(4.74 - \log 0.005) = \tfrac{1}{2}(4.74 - (\overline{3}.70))$$
$$= \tfrac{1}{2}[4.74 - (-2.30)] = \tfrac{1}{2}(4.74 + 2.30) = \tfrac{1}{2}(7.04)$$
$$= 3.52$$

B. Diprotic Acids. A diprotic acid is one which is capable of giving off two protons per unit. We shall use H_2A as the general formula for such an acid. In aqueous solution it undergoes protolysis in stages as follows:

$$H_2A + H_2O \rightleftharpoons H_3O^+ + HA^-$$
$$HA^- + H_2O \rightleftharpoons H_3O^+ + A^{--}$$
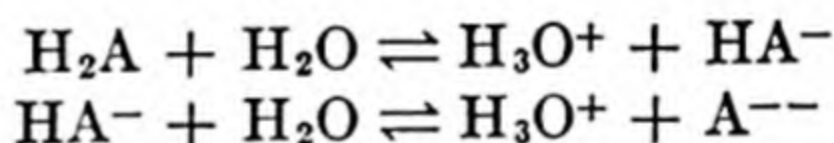
For each of the stages in this protolysis, a protolysis constant can be written.

$$K_1 = \frac{[H_3O^+][HA^-]}{[H_2A]}$$
$$K_2 = \frac{[H_3O^+][A^{--}]}{[HA^-]}$$

Values for these primary and secondary protolysis constants can be determined, and it is found that, in general, the value of K_2 is much less than that of K_1. This indicates that the extent of the secondary protolysis is much less than that of the primary stage. The reason for this is that the removal of the first proton leaves the remaining part of the acid with a greater negative charge than it had before. This exerts a stronger attractive effect upon the remaining proton, making it more difficult to remove.

TABLE 7-4. PROTOLYSIS CONSTANTS, IN WATER, OF SOME WEAK DIPROTIC ACIDS, AT 25°C.

Acid	K_1	K_2
Oxalic, $H_2C_2O_4$.............	5.4×10^{-2}	5.2×10^{-5}
Carbonic, H_2CO_3.............	4.3×10^{-7}*	4.7×10^{-11}
Hydrosulfuric, H_2S.........	9.1×10^{-8}	1.0×10^{-15}

* The value for K_1 is based on the assumption, incorrect but usually made, that when carbon dioxide is dissolved in water it is completely converted to carbonic acid.

In cases where the value of K_2 is much smaller than that of K_1, it is probably safe to assume that practically all the hydronium ions come from the primary protolysis. Therefore, in solutions of those weak diprotic acids for which this is true, we may calculate the concentration of hydronium ion by assuming that they behave as if they were monoprotic acids and use Eq. (7-12)

$$[H_3O^+] = \sqrt{K_1c}$$

The concentration of the primary ion (HA^-) will be equal approximately to the concentration of hydronium ion, since the two ions are formed in equal amounts by the primary protolysis and a very small amount of the primary ion is consumed by the secondary protolysis. This being the case, we find from the expression for K_2 that the concentration of the secondary ion (A^{--}) is

$$[A^{--}] = K_2 \qquad (7-14)$$

Example. A solution contains 0.050 mole of carbon dioxide per liter. What are the concentrations of hydronium ion, bicarbonate ion, and carbonate ion in it?

$$[H_3O^+] = [HCO_3^-] = \sqrt{K_1c} = \sqrt{4.3 \times 10^{-7} \times 5.0 \times 10^{-2}}$$
$$= 1.5 \times 10^{-4}$$
$$[CO_3^{--}] = K_2 = 4.7 \times 10^{-11}$$

3. *Equilibrium in Aqueous Solutions of Weak Bases*

A. Monoprotic Bases. Monoprotic bases are ones capable of accepting one proton per unit. The unit may be a neutral molecule (NH_3), an anion (CN^-), or a cation [$Cu(OH)(H_2O)_3^+$].

Hydroxide ion is the strongest base that can exist in significant concentration in dilute aqueous solution. In such solutions all

stronger bases pick up protons from water to leave an equivalent amount of hydroxide ions.

Every acid has a conjugate base which is derived from the acid by the removal of a proton. In Table 7-2 are listed the bases conjugate to the acids already listed. The strength of a base is inversely proportional to the strength of its conjugate acid. Thus, in Table 7-2, the strengths of the bases increase from top to bottom, so that water, the weakest acid shown, is conjugate to hydroxide ion, the strongest base shown. The bases, such as chloride ion, that are conjugate to the very strong acids, are so very weak that any proton exchange between them and water proceeds to a negligible extent.

In developing the expressions for the protolysis constant of a weak base we shall use as our typical base, A^-, which is conjugate to HA, the typical weak acid used previously. The reaction of this base with water may be represented as

$$A^- + H_2O \rightleftharpoons HA + OH^-$$
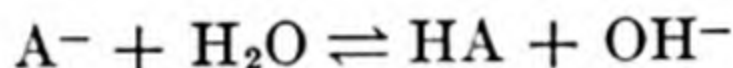
By a procedure similar to that employed for the weak acid we arrive at the following expressions for the weak base.

$$K_{eq} = \frac{[HA][OH^-]}{[A^-][H_2O]}$$

and

$$K_b = \frac{[HA][OH^-]}{[A^-]} \tag{7-15}$$

and

$$K_b = \frac{\alpha^2 c}{1 - \alpha} \tag{7-16}$$

in which K_b represents the protolysis constant for the weak base, α is the degree of protolysis, and c is the original concentration of the base.

When K_b is of the order of 10^{-4} or less we find

$$\alpha = \sqrt{\frac{K_b}{c}} \tag{7-17}$$

$$[OH^-] = \sqrt{K_b c} \tag{7-18}$$

$$pOH = \tfrac{1}{2}(pK_b - \log c) \tag{7-19}$$

Example. What is the degree of protolysis and the concentration of hydroxide ion in a 0.020 molar solution of ammonia in water?

$$\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{2.0 \times 10^{-2}}} = \sqrt{9.0 \times 10^{-4}} = 3.0 \times 10^{-2}$$

$$[OH^-] = \sqrt{1.8 \times 10^{-5} \times 2.0 \times 10^{-2}} = \sqrt{36 \times 10^{-8}} = 6.0 \times 10^{-4}$$

$$pOH = \tfrac{1}{2}(4.74 - \log 0.020) = \tfrac{1}{2}(4.74 + 1.70)$$
$$= \tfrac{1}{2}(6.44) = 3.22$$

B. Diprotic Bases. Diprotic bases are ones, such as carbonate ion (CO_3^{--}), that are capable of accepting two protons per unit. By reasoning similar to that employed in the case of weak diprotic acids we come to the conclusion that, in the case of weak diprotic bases, the acceptance of the first proton and the resulting concentration of hydroxide ion in the solution is the significant reaction. The extent to which the second proton is accepted is so small that the resulting increase in the concentration of hydroxide ion in the solution is negligible. Consequently, Eq. (7-17), Eq. (7-18), and Eq. (7-19) are satisfactory to use in calculations involving solutions of weak diprotic bases.

A useful relationship between the protolysis constants in water of any weak acid and its conjugate weak base can be derived if we multiply K_a for the weak acid, HA, by K_b for its conjugate weak base, A^-.

$$K_a K_b = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-] = K_w \quad (7\text{-}20)$$

or

$$pK_a + pK_b = pK_w = 14.00 \quad (7\text{-}21)$$

Hence, knowing the value of K_a for any weak acid, it is an easy matter to compute the value of K_b for its conjugate weak base, or vice versa. Inspection of Table 7-2 will furnish further illustrations of this relationship.

Different names for the various types of protolytic reactions in aqueous solutions so far considered have become firmly established in chemical literature. The student should familiarize himself with these names, so that he can identify a reaction, or understand what some other writer is referring to when he uses the name.

When a protolysis starts with an acid which is a cation, or a base which is an anion, the reaction is known as *hydrolysis*, K_a

(or K_b) is known as the *hydrolysis constant*, and α is known as the *degree of hydrolysis*. In all other cases the protolysis is known as *ionization*, K_a (or K_b) is the *ionization constant*, and α is the *degree of ionization*.

In the author's opinion the term hydrolysis might better be reserved for other types of reactions with water than the protolyses here considered; for example, the action of water on ethyl acetate, or on phosphorus trichloride, or in metabolism in the body.

Example 1. What is the degree of protolysis and concentration of hydronium ion in 0.040M NH$_4$Cl?

This solution contains the weak acid, NH$_4^+$. As noted previously, any reaction between chloride ion and water is negligible.

$$\alpha = \sqrt{\frac{5.6 \times 10^{-10}}{4.0 \times 10^{-2}}} = \sqrt{1.4 \times 10^{-8}} = 1.2 \times 10^{-4}$$

$$[H_3O^+] = \sqrt{5.6 \times 10^{-10} \times 4.0 \times 10^{-2}} = \sqrt{22 \times 10^{-12}} = 4.7 \times 10^{-6}$$

$$pH = \tfrac{1}{2}(9.26 - \log 0.040) = \tfrac{1}{2}(9.26 + 1.40)$$

$$= \tfrac{1}{2}(10.66) = 5.33$$

Note that this reaction would be classed as hydrolysis and α would represent the degree of hydrolysis of 0.040M NH$_4$Cl.

Example 2. What is the degree of protolysis and the concentration of hydroxide ion in 0.050M Na$_2$CO$_3$?

This solution contains the weak diprotic base, CO$_3^{--}$. The reaction between sodium ion and water is negligible.

$$\alpha = \sqrt{\frac{2.1 \times 10^{-4}}{5.0 \times 10^{-2}}} = \sqrt{42 \times 10^{-4}} = 6.5 \times 10^{-2}$$

$$[OH^-] = \sqrt{2.1 \times 10^{-4} \times 5.0 \times 10^{-2}} = \sqrt{11 \times 10^{-6}} = 3.3 \times 10^{-3}$$

$$pOH = \tfrac{1}{2}(3.67 - \log 0.050) = \tfrac{1}{2}(3.67 + 1.30)$$

$$= \tfrac{1}{2}(4.97) = 2.49$$

Note that this reaction would also be classed as hydrolysis.

4. *Equilibrium in Aqueous Solutions Containing a Weak Acid and Its Conjugate Weak Base*

The Common Ion Effect. For a weak acid, such as HA, it has been shown that the expression, $\dfrac{[H_3O^+][A^-]}{[HA]}$, has a constant value at any given temperature. It then follows that, if the concentration of either of the ions is increased, in order to maintain equilibrium the concentration of the other ion must be decreased and this is accomplished by a reversal of the protolysis of the weak acid.

Thus, if a strong acid is added to a solution of HA, the concentration of the hydronium ion is increased and, consequently,

$$\frac{[H_3O^+][A^-]}{[HA]} > K_a$$

To restore equilibrium, the reaction $HA + H_2O \rightleftharpoons H_3O^+ + A^-$ goes toward the left until once more

$$\frac{[H_3O^+][A^-]}{[HA]} = K_a$$

At equilibrium the concentration of A^- will be less than it originally was. This repression of the protolysis of HA illustrates one aspect of the phenomenon known as the *common ion effect*, which may be stated in words as follows: If to a solution of a weak acid, or a weak base, there be added a strong electrolyte having an ion in common with the weak acid or weak base, the protolysis of the weak acid or weak base is repressed, and the concentration of the ion not in common is diminished.

The reader will recall the use of this effect in qualitative analysis to control the concentration of sulfide ion obtained from the weak acid, hydrogen sulfide, by regulating the pH of the solution. We shall be interested in its use in controlling the concentration of hydronium ion in a solution of a weak acid by adding to it a salt, one of whose ions is the conjugate weak base of the weak acid.

This effect can be demonstrated qualitatively as follows. To a beaker of water add a few drops of methyl orange and enough (one or two drops) dilute acetic acid to give a red color. The methyl orange is an indicator that is red in solutions whose concentration of hydronium ion is more than about 1×10^{-4}. If, now, solid sodium acetate is added to the solution, the concentration of hydronium ion is reduced sufficiently so that the color of the indicator changes to orange. Similarly, the repression of the protolysis of ammonia may be demonstrated by using phenolphthalein as an indicator and adding solid ammonium chloride.

The extent of this effect may be calculated as follows. Solving Eq. (7-9) for the concentration of hydronium ion gives

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]} = K_a \frac{[\text{acid}]}{[\text{conjugate base}]} \qquad (7\text{-}22)$$

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]} \qquad (7\text{-}23)$$

The solution of problems using Eq. (7-22) can be greatly simplified, without any considerable sacrifice of accuracy, by making the following assumptions: (1) The acid is so weak that for all practical purposes [HA], which represents the concentration of un-ionized acid, is equal to the total concentration of acid, represented by [acid].   (2) The amount of A^- ions coming from the protolysis of the weak acid is so small as to be negligible and, therefore, the A^- ions are considered as coming entirely from the salt.   Accordingly [A^-] equals [salt], the total concentration of the dissolved salt.   On the basis of these assumptions Eq. (7-22) may be rewritten in the following extremely useful form:

$$[H_3O^+] = K_a \frac{[acid]}{[salt]} \tag{7-24}$$

or

$$pH = pK_a + \log \frac{[salt]}{[acid]} \tag{7-25}$$

Similar reasoning will lead the student to the following expressions for the concentration of hydroxide ion in a solution containing a weak base and one of its salts.

$$[OH^-] = K_b \frac{[base]}{[conjugate\ acid]} = K_b \frac{[base]}{[salt]} \tag{7-26}$$

or

$$pOH = pK_b + \log \frac{[conjugate\ acid]}{[base]} = pK_b + \log \frac{[salt]}{[base]} \tag{7-27}$$

Example 1.   What is the concentration of hydronium ion in the solution resulting from the addition of 0.10 mole of solid sodium acetate to 400 ml. of $0.50M$ acetic acid?
Use Eq. (7-24).   Concentration of acid equals 0.50, concentration of salt equals 0.25.

$$[H_3O^+] = 1.8 \times 10^{-5} \times \frac{0.50}{0.25} = 3.6 \times 10^{-5}$$

Example 2.   What is the pH of a solution which is 0.40 molar with respect to ammonia and 0.10 molar with respect to ammonium chloride?
Use Eq. (7-23).   In this case the ammonium ion is the weak acid and ammonia is its conjugate base.

$$pH = pK_a + \log \frac{[conjugate\ base]}{[acid]} = 9.26 + \log \frac{0.40}{0.10}$$
$$= 9.26 + 0.60 = 9.86$$

Mixtures Having No Ion in Common. The Salt Effect. If, to a solution of acetic acid, some potassium chloride is added, it is found that there is a slight increase in the degree of protolysis of the weak acid and in the value for its protolysis constant. This is accounted for in the following way. It has been stated that in the case of solutions of weak electrolytes, whose ionic strength was small, we could consider that the activity of the ions was equal to their concentration. Nevertheless, to be strictly accurate, we should use activities rather than concentrations in writing equilibrium expressions. Thus, for the protolysis constant for acetic acid, in place of the expression

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[HCH_3CO_2]} \tag{7-28}$$

we should use the expression

$$K_a = \frac{a_{H_3O^+} \times a_{CH_3CO_2^-}}{a_{HCH_3CO_2}} = \frac{[H_3O^+]f_{H_3O^+} \times [CH_3CO_2^-]f_{CH_3CO_2^-}}{[HCH_3CO_2]f_{HCH_3CO_2}} \tag{7-29}$$

Equation (7-29) will give the true value for the protolysis constant for acetic acid. Equation (7-28), although the one commonly used, will give a slightly inaccurate value, depending upon the magnitude of the activity coefficients f. As long as the ionic strength of the solution is small, Eq. (7-28) is satisfactory, but the addition of potassium chloride increases the ionic strength, and it then becomes necessary to use Eq. (7-29). We have seen that an increase in ionic strength causes a decrease in the activity coefficients of the ions. This is true in all except very concentrated solutions. Therefore, if the value of K_a in Eq. (7-29) is to be maintained constant, it follows that the concentrations of the ions must increase, which can be accomplished only by an increased degree of protolysis of the acetic acid. This will result in an increase in the value of the protolysis constant as defined in Eq. (7-28). This is known as the *salt effect* and will be found whenever there is an increase in the ionic strength of a solution.

The addition of sodium acetate to a solution of acetic acid will, of course, increase the ionic strength of the solution and the value of the protolysis constant and, therefore, tend to increase the degree of protolysis of the acid, but the small extent of this tendency is more than overcome by the great decrease in protolysis produced by the addition of the common ion.

5. *Equilibrium in Aqueous Solutions Containing Equivalent Quantities of a Weak Acid And a Weak Base Which Is Not Conjugate to It*

Consider an aqueous solution containing equivalent quantities of the weak acid, acetic acid, and the weak base, ammonia.

Here we have two bases, ammonia and water, competing for the protons given off by the acetic acid. The distribution of these protons between the two bases may be computed as follows:

The protolysis between acetic acid and water can be represented as

$$HCH_3CO_2 + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$$
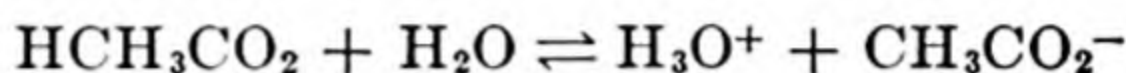
for which the protolysis constant is

$$K_a = \frac{[H_3O^+][CH_3CO_2^-]}{[HCH_3CO_2]}$$

This may be rearranged to give

$$\frac{[CH_3CO_2^-]}{[HCH_3CO_2]} = \frac{K_a}{[H_3O^+]} \tag{7-30}$$

The protolysis between acetic acid and ammonia can be represented as

$$HCH_3CO_2 + NH_3 \rightleftharpoons NH_4^+ + CH_3CO_2^-$$
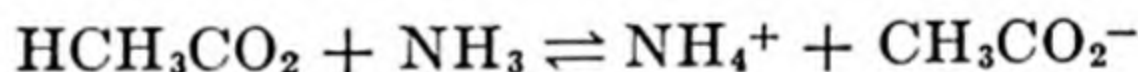
for which the equilibrium constant (in this case also the protolysis constant) is

$$K_{eq} = \frac{[NH_4^+][CH_3CO_2^-]}{[NH_3][HCH_3CO_2]} \tag{7-31}$$

If we multiply both numerator and denominator of this expression by the expression for K_w we get

$$K_{eq} = \frac{[NH_4^+][CH_3CO_2^-][H_3O^+][OH^-]}{[NH_3][HCH_3CO_2][H_3O^+][OH^-]} = \frac{K_a K_b}{K_w} \tag{7-32}$$

or

$$pK_{eq} = pK_a + pK_b - pK_w \tag{7-33}$$

where K_a and K_b are the protolysis constants for the weak acid and weak base appearing on the left side of the chemical equation for the protolytic reaction.

From Eq. (7-31) and Eq. (7-32) we find that

$$\frac{[CH_3CO_2^-]}{[HCH_3CO_2]} = \frac{K_a K_b [NH_3]}{K_w [NH_4^+]} \tag{7-34}$$

and equating the right side of this to the right side of Eq. (7-30) gives

$$\frac{K_a}{[H_3O^+]} = \frac{K_a K_b [NH_3]}{K_w [NH_4^+]}$$

or

$$\frac{[NH_4^+]}{[H_3O^+]} = \frac{K_b [NH_3]}{K_w}$$

or, in general,

$$\frac{\text{Protons given to base}}{\text{Protons given to water}} = \frac{K_b \, [\text{base}]}{1.00 \times 10^{-14}} \qquad (7\text{-}35)$$

Hence, if the expression, K_b [base], has a value of 1.00×10^{-12} the base will get 100 times as many protons as does the water, and we will introduce only a 1 per cent error if we assume that it gets them all. As the value of K_b [base] increases, the error involved in the assumption gets smaller.

Accordingly, in this case, we shall assume that the only significant reaction is that between acetic acid and ammonia. If c represents the initial concentration of each of the reactants and if x represents the extent of the protolysis, we may represent the conditions at equilibrium as

$$NH_3 + HCH_3CO_2 \rightleftharpoons NH_4^+ + CH_3CO_2^- \qquad (7\text{-}36)$$
$$c(1-x) \qquad c(1-x) \qquad cx \qquad cx$$
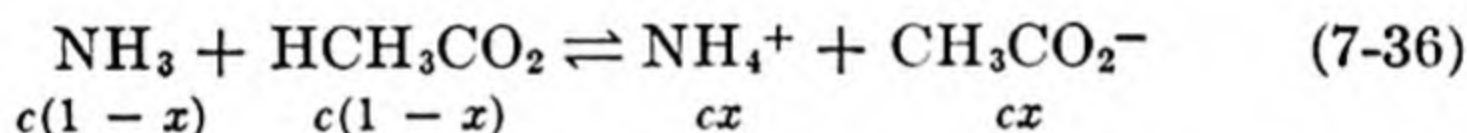
From this expression can be derived the following expressions for the equilibrium constant for the reaction.

$$K_{eq} = \frac{[NH_4^+][CH_3CO_2^-]}{[NH_3][HCH_3CO_2]} = \frac{K_a K_b}{K_w} = \frac{x^2}{(1-x)^2} \qquad (7\text{-}37)$$

Knowing the value of the equilibrium constant we can, from Eq. (7-37), compute the degree of protolysis as follows:

$$\frac{x}{1-x} = \sqrt{K_{eq}}$$

$$x = \sqrt{K_{eq}} - x\sqrt{K_{eq}}$$

$$x = \frac{\sqrt{K_{eq}}}{1 + \sqrt{K_{eq}}} \qquad (7\text{-}38)$$

An approximate idea of the degree of protolysis in any similar reaction can be gained from Table 7-5.

TABLE 7-5. RELATION BETWEEN pK_{eq} AND x FOR THE REACTION IN WATER BETWEEN EQUIVALENT QUANTITIES OF A WEAK ACID AND A WEAK BASE WHICH IS NOT CONJUGATE TO IT

pK_{eq}	−6	−4	−3	−2	−1	0	+1	+2	+3	+4	+6
x	0.999	0.99	0.97	0.91	0.76	0.50	0.24	0.09	0.03	0.01	0.001

The concentration of hydronium ion in the resulting solution may be computed as follows: From Eq. (7-36) we note that

$$[HCH_3CO_2][NH_4^+] = [NH_3][CH_3CO_2^-]$$
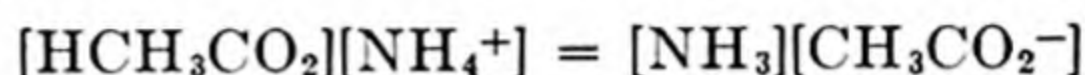
Multiplying both sides of this equation by $[H_3O^+][H_3O^+][OH^-]$ gives

$$[H_3O^+][H_3O^+][OH^-][HCH_3CO_2][NH_4^+]$$
$$= [NH_3][CH_3CO_2^-][H_3O^+][H_3O^+][OH^-]$$

which may be rearranged to give

$$[H_3O^+]^2 = [H_3O^+][OH^-]\frac{[H_3O^+][CH_3CO_2^-]}{[HCH_3CO_2]}\frac{[NH_3]}{[NH_4^+][OH^-]} = K_w\frac{K_a}{K_b}$$

or

$$[H_3O^+] = \sqrt{K_w\frac{K_a}{K_b}} \qquad (7\text{-}39)$$

or

$$pH = \tfrac{1}{2}(pK_w + pK_a - pK_b) \qquad (7\text{-}40)$$

These expressions indicate that the degree of protolysis and the resulting concentration of hydronium ion are independent of the concentration of the acid and the base, so long as they are equivalent, at least within the limits where the equations are applicable.

Example. What is the degree of protolysis and the concentration of hydronium ion in a solution containing equivalent quantities of ammonia and acetic acid?

$$K_{eq} = \frac{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}{1.00 \times 10^{-14}} = 3.2 \times 10^4$$

$$pK_{eq} = 4.74 + 4.74 - 14.00 = -4.52$$

$$x = \frac{\sqrt{3.2 \times 10^4}}{1 + \sqrt{3.2 \times 10^4}} = \frac{179}{180} = 0.994 = 99.4\%$$

$$[H_3O^+] = \sqrt{1.00 \times 10^{-14} \times \frac{1.8 \times 10^{-5}}{1.8 \times 10^{-5}}} = 1.00 \times 10^{-7}$$

$$pH = \tfrac{1}{2}(14.00 + 4.74 - 4.74) = 7.00$$

The type of calculation just discussed is applicable to a number of other situations, as will be illustrated in the following examples.

Example 1. What is the degree of protolysis and the concentration of hydronium ion in an aqueous solution of ammonium cyanide?

In solution, ammonium cyanide furnishes equal numbers of ammonium ions and cyanide ions and hence falls into the category under consideration, *i.e.*, equivalent amounts of a weak acid, NH_4^+, and a weak base, CN^-, which is not conjugate to it.

$$K_{eq} = \frac{5.6 \times 10^{-10} \times 1.4 \times 10^{-5}}{1.00 \times 10^{-14}} = 0.79$$

$$pK_{eq} = 9.26 + 4.86 - 14.00 = 0.12$$

$$x = \frac{\sqrt{0.79}}{1 + \sqrt{0.79}} = \frac{0.89}{1.89} = 0.47 = 47\%$$

$$[H_3O^+] = \sqrt{1.00 \times 10^{-14} \frac{5.6 \times 10^{-10}}{1.4 \times 10^{-5}}} = \sqrt{4.0 \times 10^{-19}} = 6.2 \times 10^{-10}$$

$$pH = \tfrac{1}{2}(14.00 + 9.26 - 4.86) = 9.20$$

Since this reaction starts with an acid which is a cation and a base which is an anion, it is sometimes classed as hydrolysis.

Example 2. What is the degree of protolysis and the concentration of hydronium ion in an aqueous solution of sodium bicarbonate?

Sodium bicarbonate, in common with the primary salts of other weak diprotic acids, furnishes an anion, HCO_3^-, which is amphiprotic, *i.e.*, both a weak acid and a weak base, reacting as follows:

$$HCO_3^- + HCO_3^- \rightleftharpoons H_2CO_3 + CO_3^{--}$$
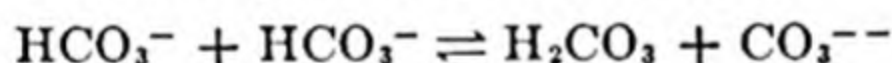
Hence, its aqueous solution falls into the category under consideration.

$$K_{eq} = \frac{4.7 \times 10^{-11} \times 2.3 \times 10^{-8}}{1.00 \times 10^{-14}} = 1.1 \times 10^{-4}$$

$$pK_{eq} = 10.33 + 7.63 - 14.00 = 3.96$$

$$x = \frac{\sqrt{1.1 \times 10^{-4}}}{1 + \sqrt{1.1 \times 10^{-4}}} = \frac{0.01}{1.01} = 0.0099 = 0.99\%$$

$$[H_3O^+] = \sqrt{1.00 \times 10^{-14} \frac{4.7 \times 10^{-11}}{2.3 \times 10^{-8}}} = \sqrt{2.0 \times 10^{-17}} = 4.5 \times 10^{-9}$$

$$pH = \tfrac{1}{2}(14.00 + 10.33 - 7.63) = 8.35$$

Since this reaction starts with a base which is an anion, it, like the preceding example, is sometimes called hydrolysis.

An expression equivalent to Eq. (7-39) which can be used in the case of primary salts of weak diprotic acids is

$$[H_3O^+] = \sqrt{K_1 K_2} \tag{7-41}$$

or

$$pH = \tfrac{1}{2}(pK_1 + pK_2) \tag{7-42}$$

in which K_1 and K_2 are the first and second protolysis constants for the weak acid.

Another group of substances whose behavior in aqueous solution falls into this same category are the ampholytes, of which glycine was mentioned in the preceding chapter as an example. This amino acid contains within its molecule equivalent amounts of a weak acid, the COOH group, and a weak base, the NH_2 group, that is not conjugate to it. The values of the protolysis constants for the acid and the base have been found[1] to be

$$K_a = 4.5 \times 10^{-3}(pK_a = 2.35)$$

and

$$K_b = 6.0 \times 10^{-5}(pK_b = 4.22)$$

When glycine is placed in aqueous solution extensive protolysis takes place, according to the reaction

$$NH_2CH_2COOH \rightleftharpoons {}^+NH_3CH_2COO^-$$
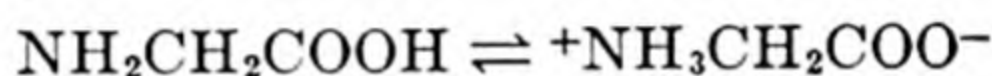
The equilibrium constant for this reaction is

$$K_{eq} = \frac{4.5 \times 10^{-3} \times 6.0 \times 10^{-5}}{1.00 \times 10^{-14}} = 2.7 \times 10^7$$

$$pK_{eq} = 2.35 + 4.22 - 14.00 = -7.43$$

The degree of protolysis is

$$x = \frac{\sqrt{2.7 \times 10^7}}{1 + \sqrt{2.7 \times 10^7}} = \frac{5,200}{5,201} = 0.9998 = 99.98\%$$

from which it appears that practically all of the glycine in solution exists in the form of the doubly charged amphion.

The concentration of hydronium ion in the solution is

$$[H_3O^+] = \sqrt{1.00 \times 10^{-14}\frac{4.5 \times 10^{-3}}{6.0 \times 10^{-5}}} = \sqrt{7.5 \times 10^{-13}} = 8.7 \times 10^{-7}$$

$$pH = \frac{1}{2}(14.00 + 2.35 - 4.22) = 6.07$$

Table 7-6 gives the values of the protolysis constants for a few amino acids. It should be noted that some writers give the values of K_a and K_b for the acid and base which are conjugate to the ones used in the preceding discussion. For example, in the case of

[1] OWEN, B. B., *J. Am. Chem. Soc.*, **56**, 24 (1934).

TABLE 7-6. PROTOLYSIS CONSTANTS IN WATER FOR SOME AMINO ACIDS AT 25°C.

pK_a	K_a	Amino acid	K_b	pK_b
2.35	4.5×10^{-3}	Glycine	6.0×10^{-5}	4.22
2.34	4.6×10^{-3}	Alanine	7.4×10^{-5}	4.13
2.33	4.7×10^{-3}	Leucine	5.6×10^{-5}	4.25
2.28	5.2×10^{-3}	Valine	5.3×10^{-5}	4.28

glycine, these alternative values would be $K_a = 1.7 \times 10^{-10}$ and $K_b = 2.2 \times 10^{-12}$. These values are for the ampholyte in the form $^+NH_3CH_2COO^-$; K_a refers to the acid group, $^+NH_3$, and K_b refers to the basic group, COO^-. In using values of the protolysis constants for the ampholytes care must be used to be sure to which form of the ampholyte the data refer.

Isoelectric Point of Ampholytes. With a few exceptions the amino acids are sparingly soluble in water. When so dissolved we have seen that the acid exists almost entirely as the amphion, $^+NH_3CH_2COO^-$, and hence will move toward neither cathode nor anode in an electrolysis. Under these conditions the ampholyte is said to be at its *isoelectric point*. The pH at the isoelectric point can be calculated by use of Eq. (7-40).

The isoelectric point is also a point of minimum solubility of the ampholyte. If, for example, solid glycine is in contact with its saturated solution, the addition of either a strong acid or a strong base will cause more glycine to dissolve. The addition of hydrochloric acid will give protons to the amphion, forming $^+NH_3CH_2-COOH$ ions which will migrate toward a cathode and will tend to form salts with any anions that may be present. The addition of sodium hydroxide will remove protons from the amphion, forming $NH_2CH_2COO^-$ ions which will migrate toward an anode and will tend to form salts with any cations that may be present.

A knowledge of the pH values for the isoelectric points of the ampholytes is useful when attempting to precipitate an ampholyte from solution. Adjustment of the pH of the solution to its isoelectric value reduces the solubility of the ampholyte to a minimum and makes its precipitation easiest.

Example. What is the pH at the isoelectric point of leucine?

$$pH = \tfrac{1}{2}(14.00 + 2.33 - 4.25) = 6.04$$

ADDITIONAL EXAMPLES OF PROTOLYTIC EQUILIBRIUMS

The first and often the most serious difficulty encountered in doing problems involving protolytic equilibrium is that of deciding which equation to apply to a given situation. The problem is not always easily recognizable as belonging to one of the categories considered earlier in this chapter. Whenever possible, it is advisable to write the equation for the chemical reaction that may take place under the conditions of the problem and then identify the conditions obtaining at equilibrium.

Example 1. Calculate the concentration of hydronium ion in a mixture formed by adding 50 ml. of $0.10M$ sodium hydroxide to 100 ml. of $0.10M$ acetic acid. The reaction that occurs under these conditions is

$$HCH_3CO_2 + OH^- \rightleftharpoons H_2O + CH_3CO_2^-$$
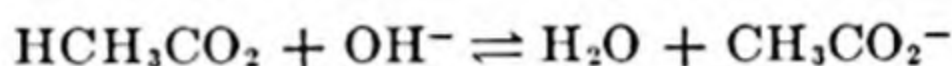
Enough base was added to neutralize half the acetic acid present. Therefore, at equilibrium we have a solution containing equal concentrations of a weak acid and its salt. It is apparent that this is a common ion effect problem.

$$[H_3O^+] = K_a \frac{[acid]}{[salt]} = 1.8 \times 10^{-5} \frac{0.033}{0.033} = 1.8 \times 10^{-5}$$

The preceding example illustrates a useful generalization: When a weak acid is half neutralized by a strong base, the concentration of hydronium ion in the solution is equal to the protolysis constant of the acid. Similarly, when a weak base is half neutralized by a strong acid, the concentration of hydroxide ion is equal to the protolysis constant of the base.

Example 2. Calculate the concentration of hydroxide ion in the solution formed by adding 50 ml. of $0.30M$ ammonium chloride to 50 ml. of $0.10M$ sodium hydroxide. The reaction that occurs under these conditions is

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$
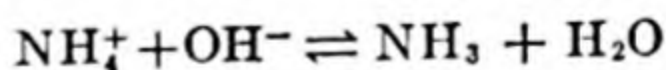
Enough sodium hydroxide was added to convert one-third of the ammonium ion to ammonia. This is also a common ion effect problem.

$$[OH^-] = K_b \frac{[base]}{[salt]} = 1.8 \times 10^{-5} \frac{0.050}{0.10} = 9.0 \times 10^{-6}$$

Using Eq. (7-23) and the proper values for pK_a and [acid] and [conjugate base] the student should calculate the pH of the solution in Example 2.

Example 3.   Calculate the pOH of the solution formed by adding 50 ml. of 0.20M acetic acid to 100 ml. of 0.10M sodium hydroxide.   In this case the amounts of acid and base are equivalent to each other.   They react to produce a 0.067 molar solution of sodium acetate, containing the weak base, acetate ion.

Use Eq. (7-19).

$$pOH = \tfrac{1}{2}(pK_b - \log c) = \tfrac{1}{2}(9.26 - \log 0.067)$$
$$= \tfrac{1}{2}(9.26 + 1.17) = 5.22$$

Example 4.   Calculate the pH of the solution formed by mixing equal volumes of 0.200M potassium cyanide and 0.200M hydrochloric acid.   Just enough acid was added to convert the cyanide ion completely to hydrocyanic acid, according to the reaction

$$H_3O^+ + CN^- \rightleftharpoons HCN + H_2O$$
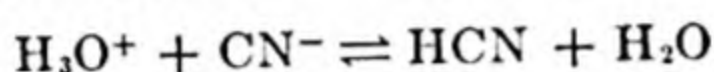
forming a 0.100 molar solution of the weak acid.

Use Eq. (7-13).

$$pH = \tfrac{1}{2}(pK_a - \log c) = \tfrac{1}{2}(9.14 - \log 0.100)$$
$$= \tfrac{1}{2}(9.14 + 1.00) = 5.07$$

EQUILIBRIUM BETWEEN A SOLID SALT AND ITS IONS IN SOLUTION.   THE SOLUBILITY-PRODUCT CONSTANT

When a slightly soluble salt, such as silver chloride, dissolves in water, we believe that the reaction can be represented as

$$AgCl \text{ (solid)} \rightleftharpoons Ag^+ + Cl^-$$
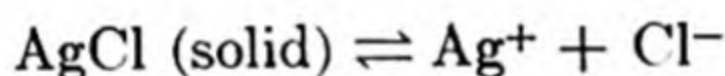
If the solution is saturated, equilibrium exists between the solid silver chloride and its ions in solution.   If the salt is only slightly soluble and the solution contains no other electrolyte, so that its ionic strength is small, then the activities of the ions are practically the same as their concentrations.   In that case we can write, as the expression for the equilibrium constant of the reaction

$$K_{eq} = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

The concentration of a solid is a constant, so that this expression may be rewritten to read

$$K_{sp} = K_{eq}[AgCl] = [Ag^+][Cl^-] \tag{7-43}$$

where K_{sp} represents the solubility-product constant of the salt.

Stated in words, the principle illustrated is: In a saturated solution of a slightly soluble electrolyte, the product of the ionic concentrations is a constant if the temperature is held constant.

In the case of more complex salts, furnishing more than one of each kind of ion per molecule, the concentration of each ion appearing in the expression for the solubility-product constant must be raised to the power corresponding to the number of those ions appearing in the reaction representing the solution of the salt. For example, in the case of silver chromate, the reaction is written

$$Ag_2CrO_4 \text{ (solid)} \rightleftharpoons 2Ag^+ + CrO_4^{--}$$
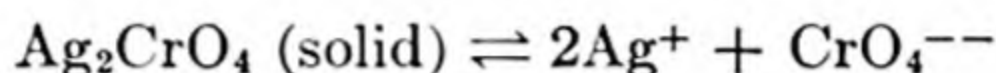
and the expression for the solubility-product constant is

$$K_{sp} = [Ag^+]^2[CrO_4^{--}] \tag{7-44}$$

If the product of the ionic concentrations in a solution is greater than the value of the solubility-product constant, solid solute will precipitate until a condition of equilibrium is reached. If, on the other hand, the product of the ionic concentrations is less than the value of the solubility-product constant, then solid solute in contact with the solution will dissolve until the solution is saturated.

Example 1. The solubility of silver chloride in water is 0.0019 g./liter. Calculate the value of the solubility-product constant for silver chloride.

First convert grams per liter to moles per liter by dividing by the molecular weight of silver chloride.

$$\frac{0.0019}{143.5} = 1.3 \times 10^{-5} \text{ mole/liter}$$

Since one silver ion and one chloride ion are formed from each molecule of silver chloride, it follows that

$$[Ag^+] = [Cl^-] = 1.3 \times 10^{-5}$$

Therefore, the value of the solubility-product constant is given by the expression

$$K_{sp} = [Ag^+][Cl^-] = (1.3 \times 10^{-5})^2 = 1.7 \times 10^{-10}$$

Example 2. The solubility of silver chromate is 8×10^{-5} mole/liter. Calculate the value of the solubility-product constant for silver chromate. Each silver chromate molecule furnishes two silver ions and one chromate ion. Therefore, we find that

$$[Ag^+] = 16 \times 10^{-5}$$

and

$$[CrO_4^{--}] = 8 \times 10^{-5}$$

Substituting these values in the expression for the solubility-product constant gives

$$K_{sp} = [Ag^+]^2[CrO_4^{--}] = (16 \times 10^{-5})^2(8 \times 10^{-5}) = 2 \times 10^{-12}$$

Example 3. What is the solubility of silver chloride in a solution of hydrochloric acid in which the concentration of chloride ion is 0.02 mole/liter?

The amount of chloride ion furnished by the silver chloride is so small compared with that furnished by the hydrochloric acid that we may neglect it in our calculations. Therefore, the concentration of silver ion in the solution will be given by the expression

$$[Ag^+] = \frac{K_{sp} \text{ for AgCl}}{[Cl^-]} = \frac{1.7 \times 10^{-10}}{2 \times 10^{-2}} = 9 \times 10^{-9}$$

Since each molecule of silver chloride furnishes one silver ion, it follows that the solubility of silver chloride is equal to the concentration of silver ion, *i.e.*, 9×10^{-9} mole/liter.

Example 4. If equal volumes of $0.00002M$ silver nitrate and $0.04M$ potassium chromate are mixed, will silver chromate precipitate?

After mixing the two solutions we find that

$$[Ag^+] = 1 \times 10^{-5}$$

and

$$[CrO_4^{--}] = 2 \times 10^{-2}$$

Substituting these values in the expression for the solubility-product constant of silver chromate gives

$$[Ag^+]^2[CrO_4^{--}] = (1 \times 10^{-5})^2(2 \times 10^{-2}) = 2 \times 10^{-12}$$

This value does not exceed that of the solubility-product constant; therefore, silver chromate will not precipitate.

Effect of Added Electrolyte on the Solubility of a Slightly Soluble Salt and on the Value of Its Solubility-product Constant

The addition of potassium nitrate to a saturated solution of silver chloride will so increase the ionic strength of the solution that the activities of the ions are no longer the same as their concentrations. To get a correct expression for the solubility-product constant, it would then be necessary to write it as follows:

$$K_{sp} = a_{Ag^+} \times a_{Cl^-} = [Ag^+]f_{Ag^+} \times [Cl^-]f_{Cl^-} \qquad (7\text{-}45)$$

The increase in ionic strength of the solution will decrease the value of the activity coefficient f for each ion. Therefore, if the value of the solubility-product constant in Eq. (7-45) is to remain constant, the concentrations of the silver ion and chloride ion must increase. In other words, the solubility of silver chloride increases and the value of the solubility-product constant as defined in Eq. (7-43) likewise increases. This result is recognizable as the salt effect.

If the added electrolyte is something, like potassium chloride, that has an ion in common with the slightly soluble salt, the salt effect will still tend to increase the value of the solubility-product constant of silver chloride, but the solubility will be decreased by the common ion effect.

If a great excess of chloride ion is added to silver chloride, the solubility of the latter will be increased because of the formation of complex ions, such as $AgCl_2^-$.

Advantage is taken of the salt effect in the dissolving of serum globulin, which is more soluble in $0.1M$ sodium chloride than it is in water.[1]   The dissolved globulin may be reprecipitated by removal of the salt and adjustment of the pH of the solution to the isoelectric point of the globulin.

Problems

1. If 2.00 moles of ethyl alcohol is added to 3.00 moles of acetic acid, how many moles each of alcohol, acid, ethyl acetate, and water will be present in the mixture at equilibrium?

2. The concentration of hydronium ion in $0.010M$ chloracetic acid is 3.7×10^{-3} mole/liter.   Calculate the value of the protolysis constant for the acid.

3. Calculate the degree of protolysis of formic acid in 0.050 molar solution.

4. Calculate the concentration of hydroxide ion in $0.30M$ ammonia.

5. Calculate the pH of a 0.010 molar solution of hydrogen sulfide. What is the concentration of sulfide ion in this solution?

6. Calculate the concentration of hydroxide ion in $0.020M$ acetic acid.

7. If 200 ml. of $0.10M$ ammonia is added to 300 ml. of $0.20M$ ammonium chloride, what is the pH of the resulting mixture?

8. What is the concentration of hydronium ion and the degree of protolysis of $0.10M$ aniline hydrochloride, which furnishes in solution the ions: $C_6H_5NH_3^+$ and Cl^-?

9. What is the degree of protolysis and the pH of an aqueous solution of aniline acetate?

10. What is the degree of protolysis and the concentration of hydronium ion in 0.050 molar solutions of each of the following salts: NaH_2PO_4, Na_2HPO_4, Na_3PO_4?

11. What is the pH of a solution containing equivalent amounts of NaH_2PO_4 and Na_2HPO_4?

12. Calculate the concentration of hydronium ion in each of the following mixtures:

   a. 100 ml. $0.15M$ acetic acid $+$ 200 ml. $0.60M$ sodium acetate.
   b. 100 ml. $0.15M$ acetic acid $+$ 100 ml. $0.075M$ sodium hydroxide.
   c. 100 ml. $0.10M$ acetic acid $+$ 50 ml. $0.15M$ sodium hydroxide.

[1] Cohn, E. J., *J. Gen. Physiol.*, **4**, 697 (1922).

d. 100 ml. 0.10M acetic acid + 100 ml. 0.10M sodium hydroxide.

e. 100 ml. 0.10M acetic acid + 150 ml. 0.10M sodium hydroxide.

f. 100 ml. 0.10M sodium acetate + 40 ml. 0.10M hydrochloric acid.

g. 100 ml. 0.10M sodium acetate + 50 ml. 0.20M hydrochloric acid.

h. 100 ml. 0.20M ammonia + 0.535 g. ammonium chloride.

i. 100 ml. 0.30M ammonia + 100 ml. 0.10M hydrochloric acid.

j. 100 ml. 0.10M ammonia + 100 ml. 0.10M hydrochloric acid.

k. 100 ml. 0.10M ammonia + 100 ml. 0.20M hydrochloric acid.

l. 100 ml. 0.10M ammonium chloride + 50 ml. 0.06M sodium hydroxide.

m. 100 ml. 0.10M ammonium chloride + 0.40 g. sodium hydroxide.

13. Calculate the pH at the isoelectric point of alanine.

14. Calculate the degree of protolysis of valine in aqueous solution.

15. What is the degree of protolysis and the pH of 0.010M potassium cyanide?

16. The solubility of lead fluoride, PbF_2, is 0.064 g. per 100 ml. of water. Calculate the value of the solubility-product constant for lead fluoride.

17. The solubility of lead chromate, $PbCrO_4$, is 0.000020 g. per 100 ml. of water. Calculate the value of the solubility-product constant for lead chromate.

18. For lead iodide, PbI_2, the value of the solubility-product constant is 1.4×10^{-8}. Calculate the solubility of lead iodide in 0.10M potassium iodide solution.

CHAPTER 8

THERMODYNAMICS

Thermodynamics is concerned with the quantitative relations between heat and the other forms of energy. A knowledge of thermodynamics is important because all other forms of energy tend to change into heat. While it is always possible to convert these other forms of energy into heat, to change heat into work is not always possible. Neither is it always possible to convert any of the other forms of energy completely into work. For example, of the total energy released in a chemical reaction some can be converted into work, but some may appear as heat given to the surroundings and this portion cannot be converted into work. A knowledge of the quantitative relations between heat and the other forms of energy, and the restrictions on the conversion of any of these forms of energy into work, is useful in understanding and predicting physical-chemical behavior.

All that we shall attempt in this chapter is to present some of the fundamental ideas of thermodynamics, to define the terms used, and to indicate some of its useful applications.

The whole science of thermodynamics is based upon three fundamental statements known as the laws of thermodynamics. The succeeding discussion will consider two of these laws, which are statements of experience, taking up their significance and some of their consequences.

The First Law of Thermodynamics

The first law of thermodynamics is sometimes known as the *law of conservation of energy*. It states that *the sum of all the energies in an isolated system is a constant.* In other words, energy may be changed from one form to another, but it can neither be created nor destroyed. This statement is not contradicted by the vast quantities of energy apparently created in nuclear fission, for we now believe that matter is one form of energy and that in the atomic bomb it is simply converted into some of its other forms.

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The relation between matter and energy was expressed by Einstein as

$$E = mc^2 \qquad (8\text{-}1)$$

in which E represents the amount of energy produced by the consumption of a mass of matter, m, and c represents the velocity of light. If m is in grams and c in centimeters per second, E will be in ergs. The velocity of light is 3.0×10^{10} cm./sec. Hence we find that 1 g. of matter is equivalent to 9.0×10^{20} ergs, or 9.0×10^{13} joules, or 2.1×10^{13} cal. It is believed that in all chemical reactions that produce energy there is a corresponding loss of mass. However, in all ordinary changes the amount of this loss in mass is so small as to be undetectable. For example, the combustion of 12 g. of carbon and 32 g. of oxygen, at 25°C., produces 94,030 cal. From this we conclude that the carbon dioxide formed should weigh 4.5×10^{-9} g. less than the sum of the weights of the carbon and oxygen.

Energy. Energy may be defined as *the capacity for doing work.* It may appear as the kinetic energy of a moving object, or it may appear as the potential energy possessed by a system because of its position or condition. Thus, a brick suspended above the earth's surface possesses potential energy because of its position. A coiled spring or a compressed gas possess potential energy because of their condition. Chemical substances may possess energy because of the arrangement of atoms and electrons within their molecules. Under appropriate conditions this energy can be converted into work or into heat.

In chemical thermodynamics we are not particularly concerned with the energy a system possesses because of its position relative to the earth's surface or because of its motion through space. We shall be concerned with the energy it possesses because of its temperature, volume, pressure, and chemical composition. This we call its *internal energy* and designate by the letter E.

It is possible to imagine each system as possessing an absolute amount of internal energy, but it is not necessary to know, nor possible to ascertain, what this absolute amount of energy is. We shall be concerned only with the *changes in internal energy* accompanying changes in temperature, volume, pressure, and chemical composition.

These changes in energy will result if a system does work or

has work done on it, or if it absorbs or gives off heat. Work is indicated by the letter w. *The value of w is positive if the system does work on its surroundings; w has a negative value if the surroundings have done work on the system.* The symbol for a heat change is q. *A positive value for q means that the system has absorbed heat from its surroundings; a negative value for q indicates that the system has given heat to its surroundings.*

Applying the first law of thermodynamics to the energy changes in a system, we can say, since energy can neither be created nor destroyed, that if a system in state 1, possessing internal energy, E_1, has heat added to it and at the same time does some work, thereby passing to state 2, in which it possesses energy, E_2, then the internal energy in the final state is equal to the internal energy in the initial state, plus the heat added to the system, minus the work done by the system.

$$E_2 = E_1 + q - w$$

or

$$\Delta E = E_2 - E_1 = q - w \tag{8-2}$$

The symbol Δ refers to a finite change. The subscript 1 refers to the initial state of the system, the subscript 2 to its final state.

The values of E_1 and E_2 and hence the value of ΔE are determined solely by the initial and final states of the system and are independent of the path followed in going from state 1 to state 2. On the other hand, the individual values of q and w are determined by the path followed and may vary widely with conditions.

The internal energy of a fixed mass of an ideal gas at constant temperature is independent of its volume. If such a gas does work in expanding isothermally it will absorb heat but, if there is no temperature change, $\Delta E = 0$, and hence the work done by the gas is exactly equal to the heat absorbed. That is, for an isothermal change in volume of an ideal gas, $q = w$.

If heat is added to an ideal gas at constant volume, so that no work of expansion is done, then $w = 0$, and hence the increase in internal energy of the gas, as evidenced by a rise in its temperature, is exactly equal to the heat absorbed.

$$\Delta E = q_v$$

The subscript refers to the fact that the volume remains constant during the change.

If a gas while being compressed is so well insulated that no heat is given to the surroundings, $q = 0$, and the increase in its internal energy is exactly equal to the work of compression done on it.

$$\Delta E = -w_q$$

The subscript is a reminder of the fact that there is no exchange of heat with the surroundings during the change. A process in which this is true is known as an *adiabatic process.*

Although in the preceding discussion we have used illustrations involving physical changes in a gas, some of the conclusions are also valid for changes involving chemical reactions. In particular, the relation $\Delta E = q_v$ holds for chemical changes, *provided that no electrical or other kind of work is done.* This states that, subject to the above-mentioned restriction, when a chemical change occurs at constant volume, the heat evolved is equal to the decrease in energy in the reaction. Since most heats of combustion are determined in a closed (constant-volume) calorimeter, the heats so measured represent changes in internal energy in the course of the reaction. Thus, for the reaction $C + O_2 \rightarrow CO_2$, for which, at 25°C., the heat of combustion at constant volume is 94,030 cal.,

$$\Delta E = q_v = -94,030 \text{ cal.}$$

The negative sign indicates that heat is evolved during the reaction. From this we conclude that the internal energy, at 25°C., of 44 g. of carbon dioxide is 94,030 cal. less than the sum of the internal energies of 12 g. of carbon and 32 g. of oxygen at the same temperature.

Reversible Process. Since many of our conclusions will be based on the assumption of a reversible process, it will be well to illustrate what we mean by the term.

Imagine a gas confined within a cylinder provided with a weightless, frictionless piston, upon which is piled some very fine sand. At the start of the experiment the piston is motionless, indicating that equilibrium exists between the pressure of the gas inside the cylinder and the combined pressure of the sand and the atmosphere outside.

Now remove one grain of sand. The gas will expand very slightly, but equilibrium will be restored almost immediately.

At no time during the process of expansion is the system very far from equilibrium. Such a change approximates an *infinitesimal change*. If the grain of sand is replaced the gas will return to its original volume—the process is *reversible*.

By the continued removal of grains of sand the gas can be allowed to undergo a finite expansion, but each step in this expansion is an infinitesimal one and can be reversed by an infinitesimal change in external conditions. At all times the system is only an infinitesimal distance away from equilibrium. A process carried out in this way is a *reversible process*. Other examples can be imagined and the concept can be extended to chemical as well as physical changes.

The ideal reversible process cannot be realized. However, some natural processes can be made to approach reversibility. One such process is that used in measuring the electrical potential of chemical cells, to be discussed in the next chapter. The concept of the reversible process permits drawing some valuable conclusions, as will be illustrated in the succeeding discussion.

Maximum Work in an Isothermal Process. Experience has shown that the *maximum* amount of work is obtained from a process only when that process is carried out *reversibly;* that this maximum amount of work, if stored somehow, is the *minimum* amount of work necessary to restore *the system and its surroundings* to their original condition; and that to carry out this restoration with the minimum amount of work it is necessary that it also be done reversibly. The statement of the first law of thermodynamics is in agreement with this experience, for if it were possible to carry out the restoration of the system and its surroundings to their original condition with a smaller amount of work than that obtained from the original process, we would have the creation of energy. It is universally true that the maximum work from any process is obtainable only when that process is carried out reversibly.

Let us now consider the maximum work obtainable from the isothermal expansion of *n* moles of an ideal gas. Let the initial state of this gas be represented by T, p, and v. Then, holding the temperature constant, let the pressure be decreased by an infinitesimal amount dp, so that the volume increases by an infinitesimal amount dv. The infinitesimal amount of work done in this volume change is equal to the pressure multiplied

by the volume change.

$$dw = (p - dp)\, dv = p\, dv - dp\, dv$$

The product of the two infinitesimals, $dp\, dv$, is negligible compared with $p\, dv$. Therefore, it can be said that the infinitesimal amount of work involved is equal to $p\, dv$ and, since the process is a reversible one, this is the maximum amount of work obtainable from the change.

$$dw_{max} = p\, dv$$

From the ideal gas equation it will be recalled that $p = nRT/v$. Therefore, for this infinitesimal change in pressure, the work done is given by the expression

$$dw_{max} = p\, dv = nRT\, \frac{dv}{v} \qquad (8\text{-}3)$$

The work done because of a finite reversible change in pressure can be considered as the sum of a series of these infinitesimal changes between the initial and final pressures. The expression for this work can be obtained by integration of Eq. (8-3). Thus, for the reversible change, at constant temperature, from p_1, v_1, to p_2, v_2, we obtain the expression

$$w_{max} = \int_{v_1}^{v_2} nRT\, \frac{dv}{v} = nRT \int_{v_1}^{v_2} \frac{dv}{v} = nRT \ln v \Big]_{v_1}^{v_2} = nRT \ln \frac{v_2}{v_1}$$
$$(8\text{-}4)[1]$$

According to Boyle's law, at constant temperature,

$$\frac{v_2}{v_1} = \frac{p_1}{p_2}$$

Therefore, Eq. (8–4) may be rewritten to read

$$w_{max} = nRT \ln \frac{p_1}{p_2} = -nRT \ln \frac{p_2}{p_1}$$

[1] The symbol ln stands for the natural logarithm, or logarithm to the base e. The value of e is 2.718. The symbol log refers to common logarithms, or logarithms to the base 10. The relation between natural logarithms and common logarithms is given by the following expression:

$$\ln x = 2.303 \log x$$

and, changing to common logarithms, this becomes

$$w_{max} = -2.303nRT \log \frac{p_2}{p_1} \qquad (8\text{-}5)$$

Equation (8-5) represents the maximum work obtainable from the isothermal expansion of n moles of an ideal gas between the initial pressure, p_1, and the final pressure, p_2. This is exactly equal to the amount of heat absorbed from the surroundings in maintaining the temperature of the gas constant. Note that if $p_2 < p_1$ the sign of w_{max} is positive, indicating that the gas does work in expanding. If $p_2 > p_1$ the sign of w_{max} is negative, indicating that work is done on the gas in compressing it.

Example. What is the maximum work obtainable from the isothermal expansion of 1 mole of an ideal gas, at 18°C., from a pressure of 4 atm. to a pressure of 1 atm.?

Using Eq. (8-5) we have

$$w_{max} = -2.303 \times 1 \text{ mole} \times 8.313 \frac{\text{joules}}{\text{mole} \times °K.} \times 291°K. \times \log \frac{1 \text{ atm.}}{4 \text{ atm.}}$$
$$= 3.36 \times 10^3 \text{ joules}$$

During this expansion an exactly equivalent amount of heat, 803 cal., will be withdrawn from the surroundings. Note that 3.36×10^3 joules is the minimum amount of work required to compress 1 mole of the gas, at 18°C., from 1 atm. to 4 atm., at the same time restoring 803 cal. to the surroundings. To accomplish this compression with this minimum amount of work it must be done reversibly.

Enthalpy. We have seen that for changes at constant volume $\Delta E = q_v$, provided that no electrical or other work is done. The restriction that no electrical or other work than that of volume change occurs will apply to the succeeding discussion unless it is specifically stated otherwise.

Changes occurring under constant pressure are more common than those occurring at constant volume, since most changes are carried out in open vessels under atmospheric pressure. Under these conditions, if the process is accompanied by a volume increase, the heat absorbed will be equal to the increase in internal energy of the system plus the heat used in effecting the volume change.

In recognition of these two factors there has been invented the term *enthalpy*, or *heat content*, of a system. Enthalpy is indicated by the symbol H and is defined by the expression

$$H = E + pv \qquad (8\text{-}6)$$

The enthalpy is a property of the system, just as is its internal energy. It is determined solely by the state of the system and not by its previous history. It is not necessary that we know the absolute values for the enthalpy of a system any more than we do for its internal energy. We shall be concerned only with changes in enthalpy.

$$\Delta H = \Delta E + \Delta pv \tag{8-7}$$

These changes depend only upon the initial and final states of the system and are independent of the path followed between them.

With the restriction of constant pressure Eq. (8-7) becomes

$$\Delta H = \Delta E + p \, \Delta v \tag{8-8}$$

Under these conditions, *i.e.*, constant pressure, and keeping in mind that no electrical or other work save that of expansion is done, the increase in enthalpy of the system is equal to the heat absorbed.

$$\Delta H = \Delta E + p \, \Delta v = q_p \tag{8-9}$$

In changes at constant pressure ΔH and q_p may be less than, equal to, or greater than ΔE, depending on the magnitude and sign of Δv.

Example 1. It requires 9713 cal. to convert 1 mole of liquid water, at 100°C. and 1 atm., to water vapor at the same temperature and pressure. What is the change in enthalpy and in internal energy in the process?

Since the process occurs at constant pressure

$$\Delta H = q_p = 9713 \text{ cal.}$$

The volume of 1 mole of liquid water, at 100°C., is 0.019 liter. The volume of 1 mole of water vapor, at 100°C. and 1 atm., is 30.1 liters. Therefore,

$$\Delta v = 30.1 - 0.019 = 30.1 \text{ liters}$$
$$p \, \Delta v = 30.1 \text{ liters} \times \text{atm.} = 728 \text{ cal.}$$
$$\Delta E = \Delta H - p \, \Delta v = 9713 - 728 = 8985 \text{ cal.}$$

Example 2. What is the heat of reaction, at constant pressure and 25°C., for the reaction

$$C \text{ (s)} + O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)}$$
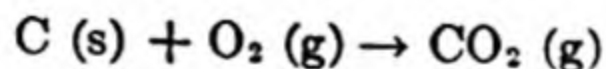
The letters in parentheses indicate the physical state of the reactants and products; (s) = solid, (g) = gas, (l) = liquid, (aq) = aqueous solution.

It is customary, in determining the value of Δv, to neglect the volumes occupied by reactants in the solid or liquid state, since these volumes are very small compared with the volumes occupied by reactants in the gaseous

state. Hence, the value of Δv will be determined by the difference in the number of moles of substance in the gaseous state on the two sides of the equation. In this case $\Delta v = 0$. Accordingly, $\Delta H = \Delta E$ and, as we have already seen that for this reaction $\Delta E = q_v = -94,030$ cal., it follows that $\Delta H = q_p = -94,030$ cal.

Example 3. The heat of reaction, at constant pressure and 25°C., for the reaction $2H_2 \text{ (g)} + O_2 \text{ (g)} \rightarrow 2H_2O \text{ (l)}$ is $\Delta H = q_p = -136,634$ cal. What is the heat of reaction at constant volume and 25°C.?

In this case there is a decrease in volume, since there are 3 moles of gas on the left side of the equation and none on the right. If we assume that the gases behave as ideal gases, then $p \, \Delta v = \Delta n \, RT$, where Δn is the change in the number of moles of gas in the reaction. In this case $\Delta n = -3$.

$$\Delta E = q_v = \Delta H - p \, \Delta v = \Delta H - \Delta n \, RT$$
$$= -136,634 \text{ cal.} - \left(-3 \text{ moles} \times 1.987 \, \frac{\text{cal.}}{\text{mole} \times \text{°K.}} \times 298\text{°K.} \right)$$
$$= -136,634 + 1,788 = -134,846 \text{ cal.}$$

THE SECOND LAW OF THERMODYNAMICS

The first law of thermodynamics states that energy may be converted from one form to another, but can neither be created nor destroyed. The second law of thermodynamics deals with the limitations governing some of the transformations of energy, particularly the transformation of the various forms of energy into work.

The second law may be stated in a variety of ways whose significance will become apparent in the succeeding discussions. Some of these statements follow.

1. *Heat passes spontaneously only from a system of higher temperature to one of lower temperature.* Passage in the opposite direction requires the expenditure of work by an outside source. For example, in the electric refrigerator the removal of heat from the cool interior to the warm room outside requires the expenditure of electrical energy in the motor.

This statement of the law indicates why we cannot use the vast stores of heat energy present in the ocean unless we can find a large reservoir having a temperature lower than that of the ocean, so that heat will flow from ocean to reservoir, some of it being converted to work in the passage.

2. *All systems tend to approach a state of maximum probability and the spontaneous changes are the ones that approach this state.* This statement of the second law, as is also true of the other statements of it, is valid only when dealing with very large num-

bers of particles. That is, the second law is a statistical law; it does not hold for the conduct of systems involving only a small number of particles. This may be illustrated in the following way.

Imagine a box divided into two equal parts by a partition which is sufficiently porous so that it imposes no restrictions on the free motion of gas molecules through it. Now assume that there are introduced into the box four molecules (a, b, c, d) of a single gas and let us see what are all the possible different ways of distributing these molecules between the two halves of the box. The student can readily demonstrate to his own satisfaction that there are sixteen different ways in which these four molecules can be so distributed. If we consider one half of the box we find that there is one way in which it contains no molecules, one way in which it contains all four molecules, four ways in which it contains one molecule, four ways in which it contains three molecules, and six ways in which it contains two molecules. In other words the state of maximum probability is one in which the molecules are evenly distributed between the two halves of the box. Note that this state of maximum probability corresponds to a state of equilibrium between the molecules in the two halves of the box and if we could measure the gas pressures on the two sides of the partition they would be equal to each other.

Now it is apparent that there will be times, in the course of their random motion, when there are three molecules on one side of the partition and only one molecule on the other side. This is a change away from the most probable state and also a change away from a state of equilibrium. It involves a large relative change away from equality of pressures on the two sides of the partition, since the pressure on one side will be three times that on the other. Such spontaneous changes in defiance of the second law are possible when dealing with small numbers of molecules.

As the total number of molecules in the box increases, the chances of the random motion of these molecules producing significant changes away from the state of maximum probability decrease rapidly. If the box contains a liter of gas at standard conditions the number of molecules is of the order of 10^{22}. Under these conditions, according to Mayer,[1] the chance of the gas pres-

[1] MAYER, JOSEPH E., and MARIA G. MAYER, "Statistical Mechanics," p. 77, John Wiley & Sons, Inc., New York, 1940.

sure on one side of the partition differing by more than one part in a million from that on the other side is one chance in $10^{10^{10}}$. In other words, the establishment of the state of maximum probability, or equilibrium, as a result of the random motion of the molecules becomes a certainty.

3. *In the course of spontaneous changes the internal energy of a system tends to become progressively less available for doing work.* This is known as the *degradation of energy.* Another way of stating this is: *the entropy of a system undergoing a spontaneous change increases.*

Entropy. The concept of entropy is one of the most elusive in physical chemistry. We shall attempt to explain its significance, to show how its value may be computed in a simple case, and then show of what use it is.

The amount of energy consumed in any change may be regarded as the product of two factors: *a capacity factor* and an *intensity factor.* If a man were given a bicycle pump and required to inflate a balloon it would probably be easy to convince him that the amount of energy he had to expend was controlled by the number of liters of air added to the balloon, *i.e.*, its change in volume (the capacity factor) and the pressure of the atmosphere against which he had to work (the intensity factor).

Energy expended = work done = $p \, \Delta v$ (in liters $\times$ atmospheres)

Perhaps not quite so obvious are the factors of the energy required to add a quantity of electricity to a system having a constant electric potential. This is the product of the number of coulombs added to the system (the capacity factor) multiplied by the potential against which it is added (the intensity factor).

Energy expended = work done = volts $\times$ coulombs = joules

Now suppose that thermal energy is expended upon a system at a constant temperature. What is added to the system? In this case the intensity factor of the energy is the absolute temperature of the system. The capacity factor is the amount of *entropy* added to the system. The symbol for entropy is S.

Thermal energy expended = $T \, \Delta S$ (in calories)

The elusiveness of entropy is enhanced by the fact that the entropy unit has no name of its own. The unit of volume is the liter; that of quantity of electricity is the coulomb; but entropy

is stated in terms of *calories per degree.* It is much as if we were compelled to state volume changes in terms of joules per atmosphere (1 liter = 101.3 joules/atm.).

The entropy of a system is a property of that system, just as are its volume, its internal energy, and its enthalpy. The entropy depends upon the state of the system and not upon the path followed in arriving at that state. Hence, changes in entropy depend only upon the initial and final states of the system and not upon the path followed between them.

The change in entropy of a system between two states having the same temperature, is defined as *the heat absorbed in going from one state to another by a reversible process, divided by the absolute temperature.* While it is possible to calculate changes in entropy when a change in temperature is involved we shall, for the sake of simplicity, limit our consideration to isothermal processes.

$$\Delta S = \frac{q_{rev}}{T} \qquad (8\text{-}10)$$

For an irreversible change, the change in entropy is the same as it is for the same process carried out reversibly, but in this case the change in entropy is always more positive than the value of the heat absorbed divided by the absolute temperature. This is so because it is only in the case of the reversible process that the maximum work is done and the maximum heat is absorbed. In irreversible processes less work is done and less heat absorbed.

$$\Delta S \text{ is more positive than } \frac{q_{irrev}}{T} \qquad (8\text{-}11)$$

Example. What is the increase in entropy when 1 mole of water, at 100°C. and 1 atm., changes to steam at the same temperature and pressure?

This change is a reversible one, since an infinitesimal decrease in temperature, or an infinitesimal increase in pressure, will cause steam to condense. We have seen in an earlier example that heat absorbed is 9713 cal. Hence,

$$\Delta S = \frac{q_{rev}}{T} = \frac{9713 \text{ cal.}}{373°K.} = 26.0 \text{ cal./°K.}$$

The increase in entropy of a system is a measure of the extent to which the internal energy of that system has become unavailable for doing work, *i.e.*, the extent of *degradation* of the energy. It is also an indication that the system is approaching a state of equilibrium.

We shall assume, for the purposes of the following discussion, that a system can never be subject to a pressure less than 1.00 atm. This is the usual circumstance for systems in contact with the atmosphere. Consider 1.00 liter of an ideal gas, at 25°C. and 2.00 atm., confined in a cylinder with a weightless, frictionless piston, and placed in contact with an inexhaustible reservoir of heat, likewise at 25°C.

As stated previously, the internal energy of the gas is determined by its pressure, volume, temperature, and chemical composition. We shall assume that in the process to be carried out the gas undergoes no chemical change and hence any changes in internal energy will be those resulting from changes in pressure, volume, and temperature.

From the ideal-gas law ($n = pv/RT$) we find that there is 0.0818 mole of gas present. Its internal energy (exclusive of that due to its chemical composition) is a function of its pv product, which is 2.00 liters $\times$ atm.

The gas is not in equilibrium with the atmospheric pressure outside the cylinder, and hence it is capable of doing some work in expanding. Now let the gas expand, isothermally and reversibly, until the pressure inside the cylinder is 1.00 atm. During this process, according to Eq. (8-5), the gas will do work,

$$w_{max} = -2.303 \ nRT \log \frac{p_2}{p_1}$$

$$= -2.303 \times 0.0818 \text{ mole} \times 1.987 \frac{\text{cal.}}{\text{mole} \times °K.}$$

$$\times 298°K. \times \log \frac{1.00 \text{ atm.}}{2.00 \text{ atm.}}$$

$$= 33.6 \text{ cal.} = 141 \text{ joules}$$

The gas will absorb this same quantity of heat, 33.6 cal., from the reservoir and, since this heat is absorbed in a reversible process, the increase in the entropy of the gas is

$$\Delta S = \frac{q_{rev}}{T} = \frac{33.6 \text{ cal.}}{298°K.} = 0.113 \text{ cal.}/°K.$$

The gas now has a volume of 2.00 liters and its internal energy is the same as it was before the expansion, since its pv product is still 2.00 liters $\times$ atm. But note that, because of our assump-

tion that the system can never be subject to a pressure less than 1 atm., the gas is now in equilibrium with its surroundings and is *incapable of doing any more work of expansion.* In other words, although the internal energy of the gas has not decreased, 33.6 cal. of that internal energy has become "degraded" or incapable of being transformed into work. The extent of this degradation is measured by the increase in entropy and is equal to $T \Delta S$. Note that the increase in entropy is also associated with the approach of the system to a state of equilibrium.

At the same time that the gas was absorbing 33.6 cal. and hence having its entropy increased by 0.113 cal./°K., the reservoir of heat lost 33.6 cal., and, since the temperature of the
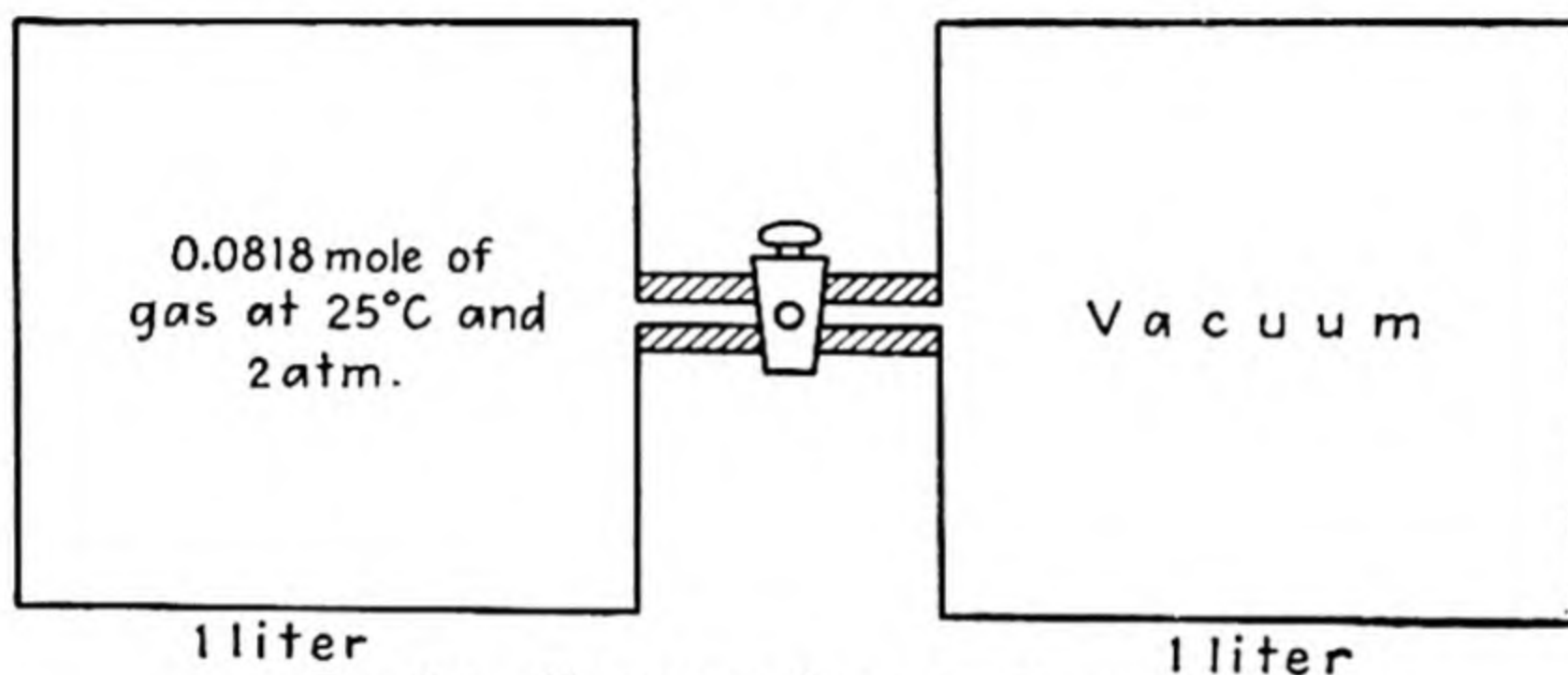
FIG. 8-1. The irreversible expansion of a gas.

reservoir was the same as that of the gas, the entropy of the reservoir decreased by 0.113 cal./°K. Accordingly, the *net change* in the entropy of the *whole system, gas plus reservoir,* was zero. This is a criterion of a reversible process, *viz.,* that for the *entire system involved*

$$\Delta S = 0 \qquad (8\text{-}12)$$

The work which the gas has done in this reversible expansion would, if it could be stored somehow, be just sufficient to restore, again by a reversible process, the entire system to its original state, *i.e.,* to compress the gas to 1.00 liter and 2.00 atm. and to return 33.6 cal. to the reservoir.

Now consider the same 0.0818 mole of ideal gas confined in one side of the container shown in Fig. 8-1 at 25°C. and 2.00 atm., and let the other side contain a vacuum. Let the apparatus be placed in a thermostat at 25°C. and let the stopcock be opened.

The gas will expand into the vacuum and the process will not be carried out reversibly. Since the gas expands against zero pressure, no work is done and no heat is withdrawn from the thermostat. Nevertheless, the gas, at the end of the expansion, will be in the same state that it was in at the end of the expansion described in the previous experiment. Therefore, since the increase in entropy is determined solely by the initial and final states of the system, we find in this case, for the gas, $\Delta S = 0.113$ cal./°K.

The thermostat has lost no heat and has undergone no other change and, hence, has lost no entropy. Therefore, the *whole system, gas plus thermostat*, has undergone an *increase in entropy*. The work which the gas might have done is lost forever; *i.e.*, that quantity of energy has become permanently degraded. This is a characteristic of an *irreversible process, viz.*, that for the *entire system involved*

$$\Delta S \text{ is positive} \tag{8-13}$$

The magnitude of ΔS is a measure of the degree of irreversibility of the process.

Although we have used physical changes in our examples illustrating entropy changes, the conclusions are applicable to chemical changes as well. Thus, if a chemical reaction can be made to proceed *reversibly* at a constant temperature and constant pressure, the heat change in the course of the reaction, when carried out in this way, is equal to the absolute temperature multiplied by the change in entropy. If, for example, an exothermic chemical change can be made to proceed reversibly under conditions of constant temperature and constant pressure, the heat released in the process is equal to the loss in entropy of the reactants multiplied by the absolute temperature. Note that this relation applies only when the reaction is carried out reversibly.

$$q_{rev} = T \Delta S \tag{8-14}$$

The heat so released will be absorbed by the surroundings and, if their temperature is the same as that of the reaction, the increase in entropy of the surroundings will equal the decrease in entropy of the reactants. Therefore, for the whole system, reaction plus surroundings, the change in entropy is zero.

If, on the other hand, the same reaction is carried out irreversibly, the decrease in the entropy of the reactants will be the same as before, but the heat evolved by the reaction will be greater. Hence, since the sign of q for an exothermic reaction is negative, we find, as stated in Eq. (8-11),

$$\Delta S \text{ is more positive than } \frac{q_{irrev}}{T}$$

or the decrease in entropy is less than the heat lost divided by the absolute temperature.

If this heat lost by the reaction is absorbed by the surroundings, we find that, since more heat is absorbed than in the case of the same process carried out reversibly, the increase in the entropy of the surroundings is greater than it was in the case of the reversible process. From this it appears that for a chemical reaction carried out irreversibly, the gain in entropy of the surroundings exceeds the loss in entropy of the reactants, or, for the whole system, reactants plus surroundings, ΔS is positive.

Free Energy

Free Energy Change in a Chemical Reaction. If a system, as the result of a chemical reaction, undergoes a decrease in internal energy, it does not necessarily follow that all of the released energy is available for doing work. Some of the energy may be unavailable and appear only as heat given to the surroundings. For reactions carried out at constant temperature, the amount of this unavailable energy is equal to the absolute temperature multiplied by the change in entropy accompanying the reaction. The maximum amount of work obtainable from the reaction (when carried out reversibly) is then given by the expression

$$w_{max} = -(\Delta E - T\,\Delta S)$$

A very crude analogy might be pointed out by referring to the case of the man inflating the balloon. The energy which he expended came from the oxidation of food in his body. Not all of the energy from this oxidation was available for doing work in inflating the balloon. Some of it appeared as heat which was dissipated directly to the surrounding air.

If a chemical reaction, as well as being carried out reversibly and at constant temperature, also occurs at constant pressure,

and if it involves an increase in volume (*e.g.*, because of the formation of a gas), then some of the maximum work available will be used up in pushing back the atmosphere.   It is only the remainder that is available for doing *useful work*, such as operating an electric motor.

$$w_{useful} = w_{max} - p \, \Delta v$$

It is this energy that can be converted into *useful work* (sometimes called *net work*) that is called the *free energy of the change* and is designated by ΔF.   The decrease in free energy during a change in a system equals the maximum amount of useful work obtainable from that change.   This maximum amount of work would be attained only under the ideal conditions of reversibility.

$$-\Delta F = w_{useful} = w_{max} - p \, \Delta v = -\Delta E + T \, \Delta S - p \, \Delta v$$

or

$$\Delta F = \Delta E + p \, \Delta v - T \, \Delta S \tag{8-15}$$

or

$$\Delta F = \Delta H - T \, \Delta S \tag{8-16}$$

It will be recalled that ΔH represents the calorimetric heat of the reaction, measured under conditions of constant pressure. It used to be thought that this represented the driving force carrying the reaction forward.   Rather it is the *decrease in free energy* that determines whether a chemical reaction under ordinary conditions (constant temperature and constant pressure) will occur spontaneously or not.   If the maximum work obtainable is just sufficient to do the work $p \, \Delta v$, involved in expanding the system against the constant pressure, then $\Delta F = 0$ and the reaction is at *equilibrium* and will go neither forward nor backward.   At this point the free energy of the reactants is exactly equal to the free energy of the products.   If ΔF has a negative value the reaction will go forward spontaneously and may be made to do useful work.   If the value of ΔF is positive the reaction will not go forward spontaneously but will require the expenditure of energy by an outside source.

The foregoing discussion can be illustrated by the following example: Consider the reaction, at 25°C., between zinc and sulfuric acid,

$$Zn \ (s) + H_2SO_4 \ (aq) \rightarrow ZnSO_4 \ (aq) + H_2 \ (g)$$
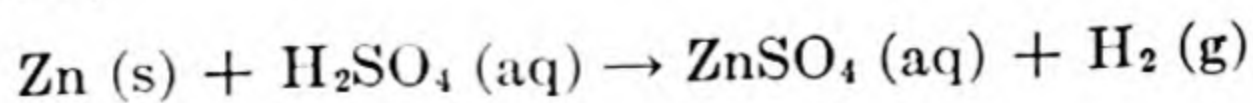
If one atomic weight of metallic zinc is allowed to react, in an open vessel, directly and irreversibly with sulfuric acid of unit activity to produce zinc sulfate at unit activity and hydrogen gas at 1 atm., the amount of heat produced is equal to the decrease in enthalpy.

$$\Delta H = q_p = -36,300 \text{ cal.}$$

From this, since the number of moles of gas formed is one, we can compute that the decrease in internal energy is

$$\Delta E = \Delta H - p \, \Delta v = \Delta H - \Delta n \, RT$$
$$= -36,300 \text{ cal.} - 1 \text{ mole} \times 1.987 \, \frac{\text{cal.}}{\text{mole} \times {}^\circ\text{K.}} \times 298^\circ\text{K.}$$
$$= -36,892 \text{ cal.}$$

This same process can be carried out reversibly in a chemical cell in which one pole consists of metallic zinc in contact with an aqueous solution of zinc sulfate of unit activity, and the other pole consists of hydrogen gas, at 1 atm., in contact with an aqueous solution of sulfuric acid of unit activity. When the process is thus carried out reversibly the heat produced in the cell is found to be 1,160 cal.

$$q_{rev} = T \, \Delta S = -1,160 \text{ cal.}$$

The difference between this value and the value $-36,300$ cal. previously cited for ΔH is due to the fact that when the process was carried out irreversibly, all of the energy, except that used up in the expansion of the system against atmospheric pressure, was converted into heat. In the reversible process that portion of the energy change that was "free" was converted into electrical work in the cell, and it was only the unavailable remnant of the released energy that appeared as heat.

The free energy change in the reaction can be computed as follows:

$$\Delta F = \Delta H - T \, \Delta S = -36,300 - (-1,160) = -35,140 \text{ cal.}$$

The decrease in entropy in the course of the reaction is

$$\Delta S = \frac{-1,160 \text{ cal.}}{298^\circ\text{K.}} = -3.9 \text{ cal./}^\circ\text{K.}$$

When the reaction is carried out reversibly the increase in entropy of the surroundings will exactly equal the loss in entropy

of the reaction. For the irreversible process the increase in entropy of the surroundings exceeds the loss in entropy of the reaction.

A knowledge of the value of the free energy change will tell whether or not a reaction is thermodynamically possible. Unfortunately, it gives no clue as to the speed with which the reaction will occur. Some reactions accompanied by a decrease in free energy take place so slowly as to be useless.

Free Energy Change When a Chemical Reaction Is Not Involved. 1. *Change of Free Energy of a Gas with Change in Pressure.* For a system, such as an ideal gas which, under isothermal decrease of pressure, does no other work than that of expansion, the decrease in free energy of the gas is equal to the maximum work of expansion done by the gas. We have seen that the amount of this work is given by Eq. (8-5), from which we conclude that the change in free energy is

$$\Delta F = -w_{max} = 2.303nRT \log \frac{p_2}{p_1} \qquad (8\text{-}17)$$

2. *Change of Free Energy of a Solute with Change in Concentration.* For a simple solute in a solution that is sufficiently dilute so that the concentration of the solute may be considered equal to its activity, the change in free energy of the solute with change in concentration is given by the expression

$$\Delta F = 2.303nRT \log \frac{c_2}{c_1} \qquad (8\text{-}18)$$

in which n represents the number of moles of solute, c_1 its initial concentration, and c_2 its final concentration.

Let us now consider the free energy change in a process involving not only concentration and pressure changes but a chemical reaction as well. We shall take the change, at a constant temperature, T, of $\frac{1}{2}$ mole of hydrogen gas, at any partial pressure, designated as p_{H_2}, into 1 mole of hydronium ion, at any concentration, designated as $[H_3O^+]$,* according to the reaction

$$\tfrac{1}{2}H_2 \, (p \text{ atm.}) + H_2O \rightarrow H_3O^+ \, (c \text{ molal}) + e$$
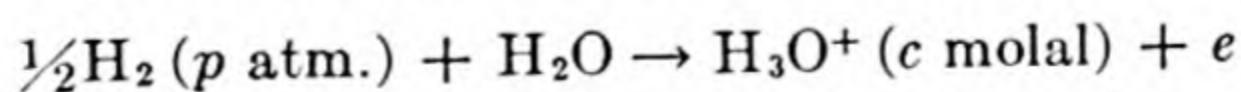
* Although the square brackets are used to indicate concentrations in moles per liter we shall assume that, in the dilute aqueous solutions considered, the difference between molarity and molality is negligible and shall not attempt to distinguish between them.

For the purpose of computing the free energy change of this process we shall break it down into three parts:

(1) $\frac{1}{2}H_2$ (p atm.) $\rightarrow \frac{1}{2}H_2$ (1 atm.)
(2) $\frac{1}{2}H_2$ (1 atm.) $+ H_2O \rightarrow H_3O^+$ ($a = 1$) $+ e$
(3) H_3O^+ ($a = 1$) $\rightarrow H_3O^+$ (c molal)

For part (1) the change in free energy is

$$\Delta F = 2.303 \times \frac{1}{2} \times RT \log \frac{1}{p_{H_2}} = 2.303 \times 1 \times RT \log \frac{1}{p_{H_2}^{\frac{1}{2}}}$$

For part (2) the value of the free energy change is unknown and will be designated simply as $\Delta F°$.

For part (3) the change in free energy is

$$\Delta F = 2.303 \times 1 \times RT \log \frac{[H_3O^+]}{1}$$

Adding together the free energy changes for all three parts gives, for the whole reaction

$$\Delta F = \Delta F° + 2.303RT \log \frac{[H_3O^+]}{p_{H_2}^{\frac{1}{2}}} \tag{8-19}$$

The fact that the value of $\Delta F°$ is unknown will probably be distressing to the student, but it does not detract from the usefulness of Eq. (8-19). $\Delta F°$ is known as the *standard free energy change, i.e.*, the free energy change involved when each substance in the reaction is in its *standard state*. The temperature ordinarily chosen for the standard state is 25°C. For gases that do not deviate greatly from ideal behavior the standard state is chosen as that in which the partial pressure of the gas is 1 atm. For pure substances that are not gases the standard state is the form (liquid or solid) that is stable at 25°C. and 1 atm. For solutes the standard state is that in which the activity of the solute is 1 molal.

We shall be concerned principally with the *differences* between the standard free energy change when hydrogen gas changes to hydronium ion and the standard free energy changes when other substances change to ions in solution. It is not necessary that we know the absolute values of $\Delta F°$, only the differences between the values of $\Delta F°$ for two reactions. These differences can be

determined experimentally.   Therefore, we can pick any reaction as our reference and assign any value we choose for its standard free energy change.   The values of the standard free energy changes for other reactions will be greater or less than this standard by a characteristic, determinable amount.   Our arbitrary standard reaction is the one already discussed, hydrogen gas going to hydronium ion, and we assign to the standard free energy change for this reaction the arbitrary value $\Delta F° = 0$.

For reactions, such as the one previously discussed, which involve a release of electrons a convenient method of measuring the free energy change is to set the reaction up so that it operates as one electrode of a voltaic cell.   If this cell can be made to operate reversibly the electrical work produced at each electrode is the maximum useful work possible from the reaction occurring at that electrode and is equal to its decrease in free energy.   Thus for the hydrogen electrode

$$\text{Electrical work} = nFE = -\Delta F = -\Delta F° - 2.303\, RT \log \frac{[H_3O^+]}{p_{H_2}^{\frac{1}{2}}}$$

The symbol F in the term nFE represents 1 faraday (96,500 coulombs) of electricity, E represents the potential of the electrode in volts, and n represents the number of equivalents involved in the electrode reaction; this is also the number of electrons shown in the balanced equation for the electrode reaction.

Free Energy Change and Equilibrium Constant.   It will be noted in Eq. (8-19) that the logarithmic term has the form of the expression for the equilibrium constant for the reaction involved,

$$\tfrac{1}{2}H_2 + H_2O \rightleftharpoons H_3O^+ + e$$
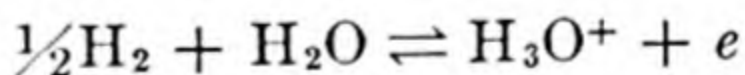
Equation (8-19) is a specific example of a general equation applicable to any reversible reaction.   The general equation is

$$\Delta F = \Delta F° + 2.303RT \log Q \qquad (8\text{-}20)$$

in which Q has the form of the expression for the equilibrium constant for the reaction in question.

When the equilibrium values for the concentration of hydronium ion and for the partial pressure of hydrogen gas are substituted in the logarithmic term in Eq. (8-19), its value then becomes that of the equilibrium constant, K, for the reaction.   Now,

recalling that for a reaction at equilibrium the change in free energy is zero, we find

$$-\Delta F = 0 = -\Delta F° - 2.303RT \log K$$

or

$$\Delta F° = -2.303RT \log K \qquad (8\text{-}21)$$

where K is the equilibrium constant for the reaction.

Equation (8-21) is applicable not only to any electrode reaction but to any reversible reaction. Thus we find that a knowledge of the values for free energy changes enables us not only to compute electrode potentials, but also to calculate equilibrium constants. Conversely, equilibrium-constant data and electrode potentials can be used to compute the values for free energy changes.

For the purpose of computing free energy changes in chemical reactions it is useful to assign values for the free energy content of substances. In doing this the following arbitrary assumptions are made: the free energy of all elements in their standard state is zero; the standard free energy change for the change of hydrogen gas to hydronium ion is zero.

We can ascertain the change in free energy when a compound or ion is formed from its elements and we assign this value as the free energy of formation of the compound or ion. For example, in the formation of 1 mole of silver chloride from its elements, according to the reaction

$$Ag + \tfrac{1}{2}Cl_2 \rightarrow AgCl$$
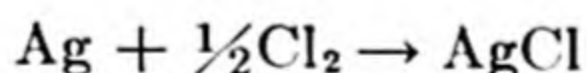
when all the substances are in their standard states, the free energy change, $\Delta F°$, is $-26{,}220$ cal. Hence, we say that the free energy of formation of silver chloride, in its standard state, is $\Delta F° = -26{,}220$ cal./mole. Tables of these values for the standard free energy of formation are available in reference books of physical chemistry. See, for example, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," by Wendell M. Latimer, Prentice-Hall, Inc., New York, 1938, from which the values given in Table 8-1 are quoted.

In reactions involving compounds or ions the change in free energy of the reaction is found by subtracting the sum of the free energy of formation of the reactants from that of the products.

TABLE 8-1. STANDARD FREE ENERGIES OF FORMATION OF SOME SUBSTANCES, IN CAL./MOLE, AT 25°C.

Substance	$\Delta F°$
Ba^{++}	$-133,850$
$BaCO_3$ (s)	$-271,570$
Br^-	$-24,578$
Ca^{++}	$-132,700$
$CaCO_3$ (s)	$-270,430$
CO (g)	$-33,010$
CO_2 (g)	$-94,450$
CO_3^{--}	$-126,390$
HCH_3CO_2 (aq)	$-96,210$
$CH_3CO_2^-$	$-89,720$
Cl^-	$-31,330$
I^-	$-12,333$
NH_3 (g)	$-3,940$
NH_3 (aq)	$-6,330$
NH_4^+	$-18,960$
H_2O (l)	$-56,690$
H_3O^+	$-56,690$ *
OH^-	$-37,585$

* This value is not quoted from Latimer but is based on the assumption that the standard free energy change for the reaction $\frac{1}{2}H_2 + H_2O \rightleftharpoons H_3O^+ + e$ is zero.

Note that these values of $\Delta F°$ refer to the free energies of formation, at 25°C., of the substances named, in their standard states, from their elements, likewise in their standard states. It is assumed that all ions are in aqueous solution.

The free energy of formation of many metallic ions can be calculated from the values of their standard electrode potentials, given in the next chapter.

Example 1. What is the electrode potential, at 25°C., developed by the reaction, $2Cl^- \rightleftharpoons Cl_2 + 2e$, when each substance is in its standard state? Table 8-1 shows that the standard free energy of formation of chloride ion is $-31,330$ cal./mole. Note that the reaction in question is the transformation of two moles of chloride ion into chlorine gas. Therefore, the value of ΔF for the reaction is $+62,660$ cal.

Using the equation $\Delta F = -nFE$ we find, since $n = 2$,

$$+62,660 \text{ cal.} = -2 \times 96,500 \times E \text{ volt} \times \text{coulombs (or joules)}$$

Before solving this equation both sides must be expressed in the same units. The left-hand side can be converted to joules by multiplying by 4.1833 joules/cal. We then have

$$+62,660 \times 4.1833 \text{ joules} = -2 \times 96,500 \times E \text{ joules}$$

from which
$$E = -1.36 \text{ volts}$$

Example 2. Compute the value of the protolysis constant, at 25°C., for the reaction, NH_3 (aq) $+ H_2O \rightleftharpoons NH_4^+ + OH^-$.

From the values in Table 8-1 we find that the standard free energy change for the reaction is $+6,475$ cal./mole. Using the expression,

$$\Delta F° = -2.303RT \log K$$

and expressing R in calories per mole per degree Kelvin, we find

$$+6,475 \frac{\text{cal.}}{\text{mole}} = -2.303 \times 1.987 \frac{\text{cal.}}{\text{mole} \times °K.} \times 298°K. \times \log K$$

from which $\log K = -4.74 = \bar{5}.26$ and $K = 1.8 \times 10^{-5}$.

Example 3. Compute the value of the solubility product constant, at 25°C., for silver chloride. The reaction is $AgCl$ (s) $\rightleftharpoons Ag^+ + Cl^-$. The standard free energy of formation of silver ion is $+18,440$ cal./mole. The standard free energy change for the reaction is then

$$\Delta F° = +18,440 + (-31,330) - (-26,220) = +13,330 \text{ cal./mole}$$

Substituting this value in the expression $\Delta F° = -2.303RT \log K$ gives $\log K = -9.77 = \overline{10}.23$ and $K = 1.7 \times 10^{-10}$

Problems

1. For the combustion of benzene, at 25°C. and constant pressure, according to the reaction

$$C_6H_6 \text{ (l)} + 7\tfrac{1}{2}O_2 \text{ (g)} \rightarrow 6CO_2 \text{ (g)} + 3H_2O \text{ (l)} \qquad \Delta H = -781,400 \text{ cal.}$$
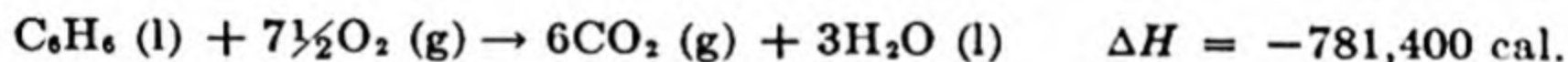
What is the value of ΔE for the reaction?

2. Using the value of ΔE obtained in Prob. 1, calculate how much less than the reactants the products of the reaction should weigh.

3. What is the minimum amount of work necessary to compress 2.5 moles of gas, isothermally at 20°C., from a pressure of 2.0 atm. to a pressure of 3.0 atm.? How many calories will be given off by the gas to its surroundings during this compression?

4. The normal boiling point of benzene is 80.1°C. At this temperature its heat of evaporation is 7,353 cal./mole. What is the value of ΔE, at 80.1°C. and 1 atm., for the reaction C_6H_6 (l) $\rightarrow C_6H_6$ (g)? Assume that benzene vapor behaves as an ideal gas. What is the value of ΔS for the same reaction?

5. What is the decrease in entropy of the gas during the change described in Prob. 3?

6. What is the increase in free energy of the gas during the change described in Prob. 3? Note that the internal energy of the gas does not increase, but more of it becomes available for doing useful work.

7. What is the change in free energy, at 25°C., for the following reaction:

$$H_2 \text{ (2 atm.)} + 2H_2O \rightleftharpoons 2H_3O^+ \text{ (0.3}m) + 2e$$
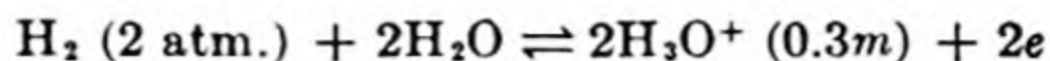
What is the potential developed by an electrode at which this reaction takes place?

8. What is the change in free energy, at 25°C., for the following reaction:

$$Ca^{++} \text{ (0.05}m) \rightleftharpoons Ca^{++} \text{ (0.25}m)$$
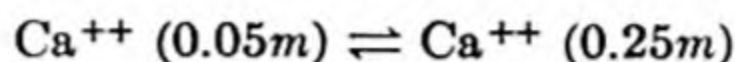
9. What is the change in free energy, at 25°C., for the following reaction:

$$Cl_2 \text{ (0.4 atm.)} + 2e \rightleftharpoons 2Cl^- \text{ (0.1}m)$$
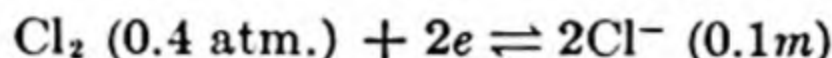
10. What should be the potential developed, at 25°C., by the electrode at which the following change occurs:

$$Ba \text{ (s)} \rightleftharpoons Ba^{++} \text{ } (a = 1) + 2e$$
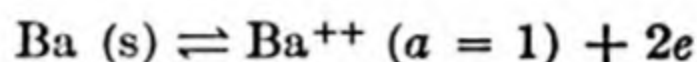
11. What is the value, at 25°C., of the protolysis constant for the following reaction:

$$HCH_3CO_2 \text{ (aq)} + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$$
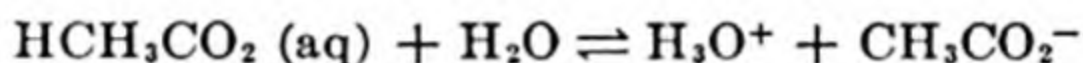
12. What is the value, at 25°C., of the solubility product constant for $BaCO_3$?

13. What is the value, at 25°C., of the solubility product constant for AgI? For AgI (s) the value of $\Delta F°$ is −15,810 cal./mole.

14. Give the value of the equilibrium constant, at 25°C., for the reaction

$$N_2 \text{ (g)} + 3H_2 \text{ (g)} \rightleftharpoons 2NH_3 \text{ (g)}$$
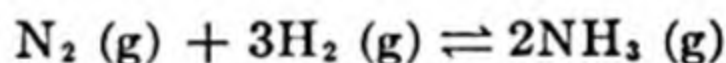
15. For the reaction $2Mg \text{ (s)} + O_2 \text{ (g)} \rightarrow 2MgO \text{ (s)}$, at 25°C., the calorimetric heat of combustion at constant volume is $q_v = -287,447$ cal. What is the change in enthalpy in the reaction? The change in entropy in the reaction is $\Delta S = -51.23$ cal./°K. What is the change in free energy in the reaction?

16. From the data in Table 7-2, calculate the value of the standard free energy change for the reaction $HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{--}$. Using this value and the data in Table 8-1, calculate the standard free energy of formation of bicarbonate ion.

CHAPTER 9

HYDRONIUM ION

If physiologists were asked to name the most important single ion encountered in their work, it is probable that most of them would select the hydronium ion. All biological processes are affected in marked degree by the acidity or alkalinity of the medium in which they occur. It becomes, therefore, of considerable importance to be able to measure accurately the concentration of hydronium ion in a solution, and also to be able to regulate this concentration.

THE DETERMINATION OF THE CONCENTRATION OF HYDRONIUM ION

The two most commonly used means for determining the concentration of hydronium ion in a solution are the method employing electromotive-force measurements and the method employing indicators. The first method is the fundamental one, upon which the other method depends.

I. Electromotive-force Measurements

The Hydrogen Electrode

The use of the hydrogen electrode for measuring the concentration of hydronium ion is based on the reaction that takes place when hydrogen gas comes in contact with water. This reaction may be represented as follows:

$$\tfrac{1}{2}H_2 + H_2O \rightleftharpoons H_3O^+ + e \tag{9-1}$$
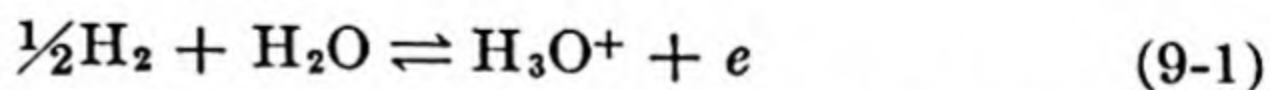
If a strip of platinum, coated with platinum black, is placed in contact with the gas and the solution (Fig. 9-1), it is found that the gas is dissolved in the surface of the platinum and, if the reaction in Eq. (9-1) proceeds forward, the electrons that are released remain on the metal, giving it a negative charge, while the positively charged hydronium ions appear in the aqueous solution. This hydrogen electrode is expressed conventionally as

$$Pt + H_2 \mid H_3O^+$$

203
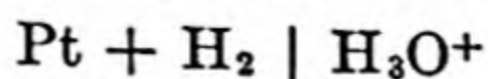
The vertical line in this expression indicates the boundary between two phases in the electrode.   In the hydrogen electrode this boundary is between the liquid phase containing hydronium ions and the solid platinum phase containing dissolved hydrogen.
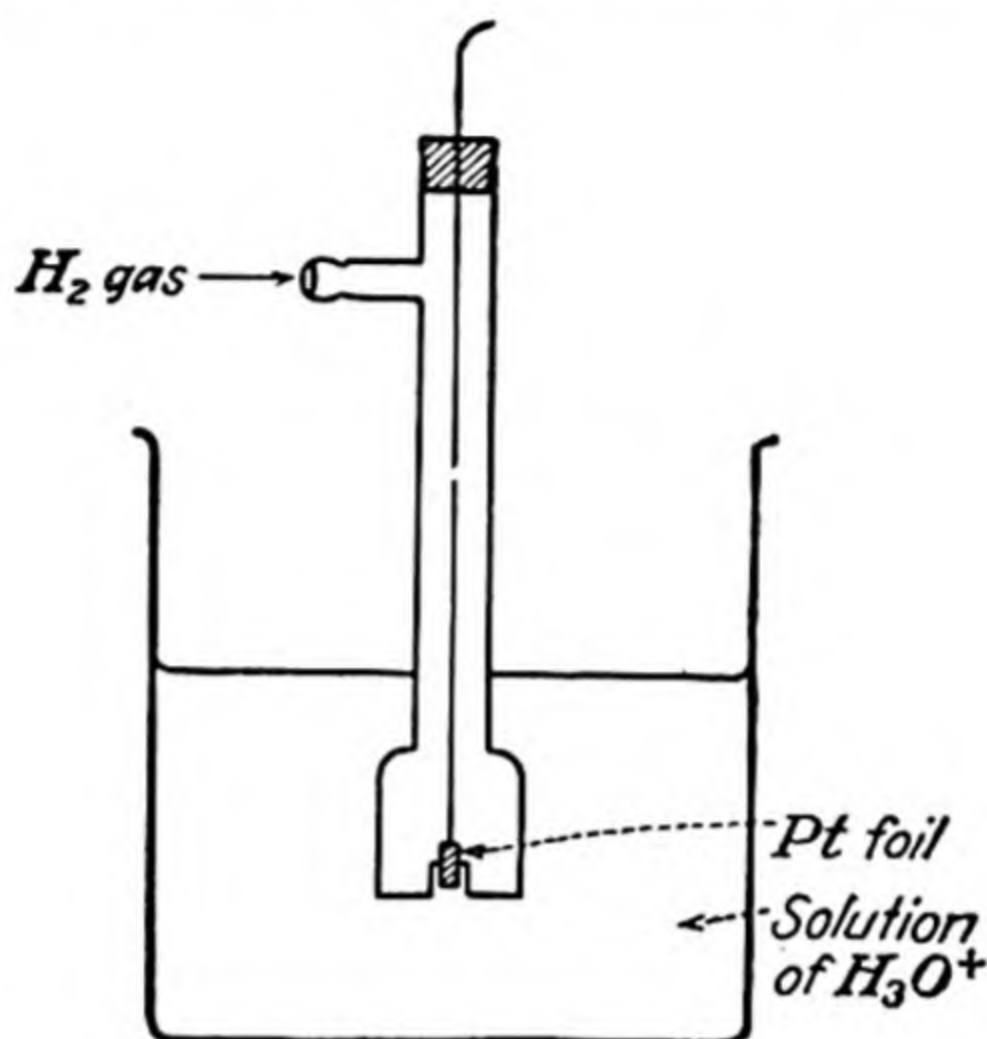
FIG. 9-1.   A hydrogen electrode.

We have seen, in Chap. 8, that for the reaction shown in Eq. (9-1) the change in free energy is related to the maximum electrical work obtainable as follows:

$$nFE = -\Delta F° - 2.303RT \log \frac{[H_3O^+]}{p_{H_2}^{\frac{1}{2}}}$$

from which we find that the potential, E, of the electrode is

$$E = \frac{-\Delta F°}{nF} - 2.303 \frac{RT}{nF} \log \frac{[H_3O^+]}{p_{H_2}^{\frac{1}{2}}} \qquad (9\text{-}2)$$

In Eq. (9-2) the term $-\Delta F°/nF$ represents the potential corresponding to the standard free energy change for the reaction, *i.e.*, the potential developed when hydrogen gas, at 1 atm., is changed into hydronium ion at an activity of 1 molal.   This is known as the *standard electrode potential* and is designated as $E°$. Equation (9-2) may be rewritten to read

$$E = E° - 2.303 \frac{RT}{nF} \log \frac{[H_3O^+]}{p_{H_2}^{\frac{1}{2}}} \qquad (9\text{-}3)$$

Since, for the reaction shown in Eq. (9-1) we have arbitrarily assigned the value zero to the standard free energy change ($\Delta F^\circ = 0$), it follows that for the hydrogen electrode the standard electrode potential is likewise zero ($E^\circ = 0$).

The hydrogen electrode in which hydrogen gas is at 1 atm. pressure and hydronium ion is at unit activity is known as the *normal hydrogen electrode.* Its potential is 0.0 volt.

Variations in the value of E above or below the value of E° are a function of the changes in the concentration of hydronium ion and in the partial pressure of hydrogen gas. If, therefore, the pressure of hydrogen gas is held constant at some known value, then measurements of E will enable us to calculate the concentration of hydronium ion. The value of E can be measured experimentally by methods that will be described later.

Equation (9-3) may be simplified by substituting the numerical values of R and F.

$$R = 8.314 \frac{\text{volt} \times \text{coulombs}}{\text{mole} \times {}^\circ\text{K.}}$$

$$F = 96{,}500 \text{ coulombs}$$

Substitution of these values in Eq. (9-3) gives

$$E = E^\circ - 0.000198 \frac{T}{n} \log \frac{[\text{H}_3\text{O}^+]}{p_{\text{H}_2}^{1/2}} \tag{9-4}$$

For the electrode reaction written in Eq. (9-1) the value of n is 1. Measurements of electrode potentials are quite commonly made at 25°C. (298°K.). Substitution of these values in Eq. (9-4) gives, for the hydrogen electrode at 25°C.,

$$E = E^\circ - 0.059 \log \frac{[\text{H}_3\text{O}^+]}{p_{\text{H}_2}^{1/2}} \tag{9-5}$$

If, as is usually the case, the partial pressure of hydrogen is maintained at 1 atm., Eq. (9-5) may be simplified to the following expression for the potential of the hydrogen electrode when the temperature is 25°C. and the partial pressure of hydrogen is 1 atm.:

$$E = E^\circ - 0.059 \log [\text{H}_3\text{O}^+] \tag{9-6}$$

Equations (9-3) to (9-5) are specific forms of a general equation which is applicable to any reversible reaction in which electrons

are released. The corresponding forms of the general equation
are

$$E = E° - 2.303 \frac{RT}{nF} \log Q \tag{9-7}$$

or

$$E = E° - 0.000198 \frac{T}{n} \log Q \tag{9-8}$$

or, at 25°C.,

$$E = E° - \frac{0.059}{n} \log Q \tag{9-9}$$

In these equations, n is the number of equivalents of substance
undergoing change, and is also the number of electrons released
in the reaction as written; Q has the form of the expression for the
equilibrium constant of the electrode reaction; and $E°$ is the
standard electrode potential, *i.e.*, the potential corresponding to
the standard free energy change for the reaction when all the
substances are in their standard states and hence the value of
$Q = 1$.

$$E° = \frac{-\Delta F°}{nF} \tag{9-10}$$

By combining Eq. (9-10) with Eq. (8-21) we obtain the follow-
ing expression for the relation between the standard electrode
potential for a reaction and its equilibrium constant:

$$\log K = \frac{nFE°}{2.303RT} \tag{9-11}$$

At 25°C. Eq. (9-11) may be simplified to

$$\log K = \frac{nE°}{0.059} \tag{9-12}$$

The value of $E°$ for any particular electrode reaction may be
determined experimentally by comparing the potential of that
electrode with the potential of the normal hydrogen electrode,
which has arbitrarily been assigned the value $E = 0.0$ volt. It
is only for the hydrogen electrode that the value of the standard
electrode potential is zero; for other electrodes the value is greater
or less than zero.

Probably the greatest confusion in working with electrode
potentials arises from the interpretation of the signs attached to

the values of E. To minimize this confusion it is necessary to establish certain conventions and to adhere to them rigidly. Different writers have adopted different sets of conventions. Any one of these is satisfactory, as long as it is thoroughly understood and is used consistently. In this text we shall use the following set of conventions:

1. The reaction taking place at the electrode is always written so that electrons are released on the right-hand side of the reaction.

2. The expression for Q is always written as the product of the concentrations, or pressures, of those substances appearing on the right-hand side of the equation divided by those appearing on the left-hand side.

3. The sign of E resulting from the calculations indicates the electron pressure on the electrode compared with that on the normal hydrogen electrode. A positive value of E indicates a greater electron pressure than that on the normal hydrogen electrode. A negative value of E indicates a smaller electron pressure than that on the normal hydrogen electrode.

Example 1. Calculate the potential, at 10°C., of the following electrode:

$$Pt + H_2 \text{ (0.50 atm.)} \mid H_3O^+ \text{ (2.0m)}$$

The electrode reaction is

$$\tfrac{1}{2}H_2 + H_2O \rightleftharpoons H_3O^+ + e$$
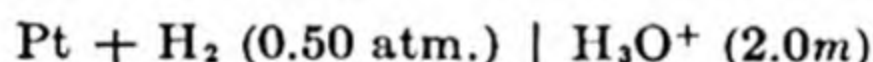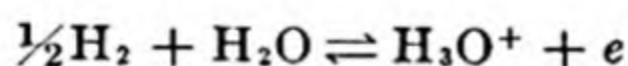
from which we find that

$$n = 1 \quad \text{and} \quad Q = \frac{[H_3O^+]}{p_{H_2}^{\frac{1}{2}}}$$

Using Eq. (9-4) we have

$$E = E° - 0.000198 \times \frac{283}{1} \times \log \frac{2.0}{0.50^{\frac{1}{2}}}$$
$$E = 0.0 - 0.056 \log 2.8$$
$$E = -0.056 \times 0.45$$
$$E = -0.025 \text{ volt}$$

The negative value of E indicates that this electrode has a smaller pressure of electrons than that on the normal hydrogen electrode.

It should be noted that this same problem can be worked out on the basis of the following electrode reaction to give the same answer:

$$H_2 + 2H_2O \rightleftharpoons 2H_3O^+ + 2e$$
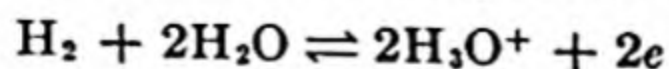
In this case, $n = 2$ and $Q = \dfrac{[H_3O^+]^2}{p_{H_2}}$

Using Eq. (9-8) we have

$$E = E° - 0.000198 \times \frac{283}{2} \times \log \frac{2.0^2}{0.50}$$
$$E = 0.0 - 0.028 \log 8.0$$
$$E = -0.028 \times 0.90$$
$$E = -0.025 \text{ volt}$$

Example 2.　The potential, at 25°C., of the following electrode is +0.030 volts.　Calculate the concentration of hydronium ion in the solution.

$$Pt + H_2 \text{ (1.0 atm.)} \mid H_3O^+$$
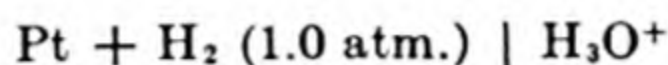
Since the temperature is 25°C. and the partial pressure of hydrogen is 1 atm., we can use Eq. (9-6).

$$+0.030 = 0.0 - 0.059 \log [H_3O^+]$$
$$\log [H_3O^+] = \frac{+0.030}{-0.059} = -0.51 = \bar{1}.49$$
$$[H_3O^+] = 0.31$$

What is the pH of this solution?

Example 3.　The potential of the following electrode, at 25°C., is −1.341 volts.　Calculate the value of the standard electrode potential for this electrode.

$$C + Cl_2 \text{ (1.0 atm.)} \mid Cl^- \text{ (2.0}m\text{)}$$

The electrode reaction is

$$2Cl^- \rightleftharpoons Cl_2 + 2e$$
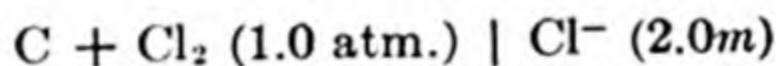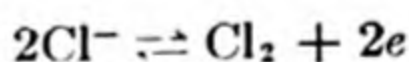
from which it appears that $n = 2$ and $Q = \dfrac{p_{Cl_2}}{[Cl^-]^2}$

Since the temperature is 25°C., Eq. (9-9) may be used.

$$-1.341 = E° - \frac{0.059}{2} \times \log \frac{1.0}{4.0}$$
$$-1.341 = E° - 0.0295(-0.602)$$
$$E° = -1.341 - 0.018 = -1.359 \text{ volts}$$

Example 4.　The value of the standard electrode potential for the zinc electrode is +0.758 volt.　Calculate the potential, at 15°C., of the following electrode:

$$Zn° \mid Zn^{++} \text{ (0.001}m\text{)}$$

The electrode reaction is

$$Zn° \rightleftharpoons Zn^{++} + 2e$$
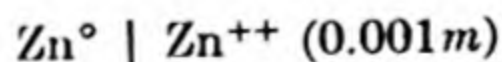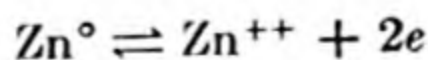
from which $n = 2$, and, since metallic zinc is already in its standard state with an activity of 1, $Q = [Zn^{++}]$.

Using Eq. (9-8) gives

$$E = +0.758 - 0.000198 \times \frac{288}{2} \times \log 0.001$$
$$E = +0.758 - 0.285(-3.0) = +0.758 + 0.0855$$
$$E = +0.844 \text{ volt}$$

Example 5. What is the value of the standard free energy change and the value of the equilibrium constant for the reaction $Zn^\circ \rightleftharpoons Zn^{++} + 2e$?

From Eq. (9-10) $\Delta F^\circ = -nFE^\circ$

$$\Delta F^\circ = -2 \times 96,500 \times 0.758 \text{ joules}$$
$$\Delta F^\circ = -146,300 \text{ joules}$$
$$\Delta F^\circ = -35,000 \text{ cal.}$$

From Eq. (9-12)

$$\log K = \frac{nE^\circ}{0.059} = \frac{2 \times 0.758}{0.059} = 25.7$$
$$K = 5 \times 10^{25}$$

Note that in this case the equilibrium constant, K, is equal to the concentration of zinc ion that is in equilibrium with metallic zinc.

TABLE 9-1. STANDARD ELECTRODE POTENTIALS, IN VOLTS, FOR SOME ELECTRODES, AT 25°C.

Electrode	Reaction	E°
$K^\circ \mid K^+$	$K^\circ \rightleftharpoons K^+ + e$	$+2.922$
$Na^\circ \mid Na^+$	$Na^\circ \rightleftharpoons Na^+ + e$	$+2.712$
$Mg^\circ \mid Mg^{++}$	$Mg^\circ \rightleftharpoons Mg^{++} + 2e$	$+2.34$
$Zn^\circ \mid Zn^{++}$	$Zn^\circ \rightleftharpoons Zn^{++} + 2e$	$+0.758$
$Sn^\circ \mid Sn^{++}$	$Sn^\circ \rightleftharpoons Sn^{++} + 2e$	$+0.14$
$Pt + H_2 \mid H_3O^+$	$H_2 + 2H_2O \rightleftharpoons 2H_3O^+ + 2e$	±0.000
$Cu^\circ \mid Cu^{++}$	$Cu^\circ \rightleftharpoons Cu^{++} + 2e$	-0.345
$Ag^\circ \mid Ag^+$	$Ag^\circ \rightleftharpoons Ag^+ + e$	-0.799
$C + Cl_2 \mid Cl^-$	$2Cl^- \rightleftharpoons Cl_2 + 2e$	-1.359

In all the preceding discussions it is to be understood that more accurate results are obtained when activities are used instead of concentrations. In dealing with dilute aqueous solutions we have assumed that the difference between activity and concentration and the difference between molality and molarity are negligible.

Cell Potentials. Reference Electrodes

It has not been found possible to measure the potential of a single electrode. In practice, the method used is to measure the potential difference between two electrodes. Then, if one of

these electrodes is taken as a standard, the potential of the other electrode with reference to the standard can be ascertained.

The Hydrogen Electrode. The most obvious choice for a standard electrode is the normal hydrogen electrode, which has been assigned the arbitrary potential of 0.0 volt. A typical cell employing this electrode is illustrated in Fig. 9-2. To conserve space, this cell is represented conventionally as follows:

$$Pt + H_2 \text{ (1 atm.)} \mid H_3O^+ \text{ (1.0}m\text{)} \parallel KCl \parallel H_3O^+ \text{ (?}m\text{)} \mid H_2 \text{ (1 atm.)} + Pt$$
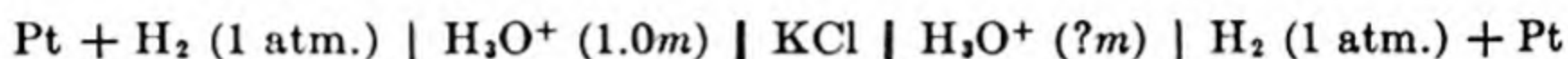
The double vertical lines ‖ are used to indicate the boundary between two solutions of different composition in the same solvent.
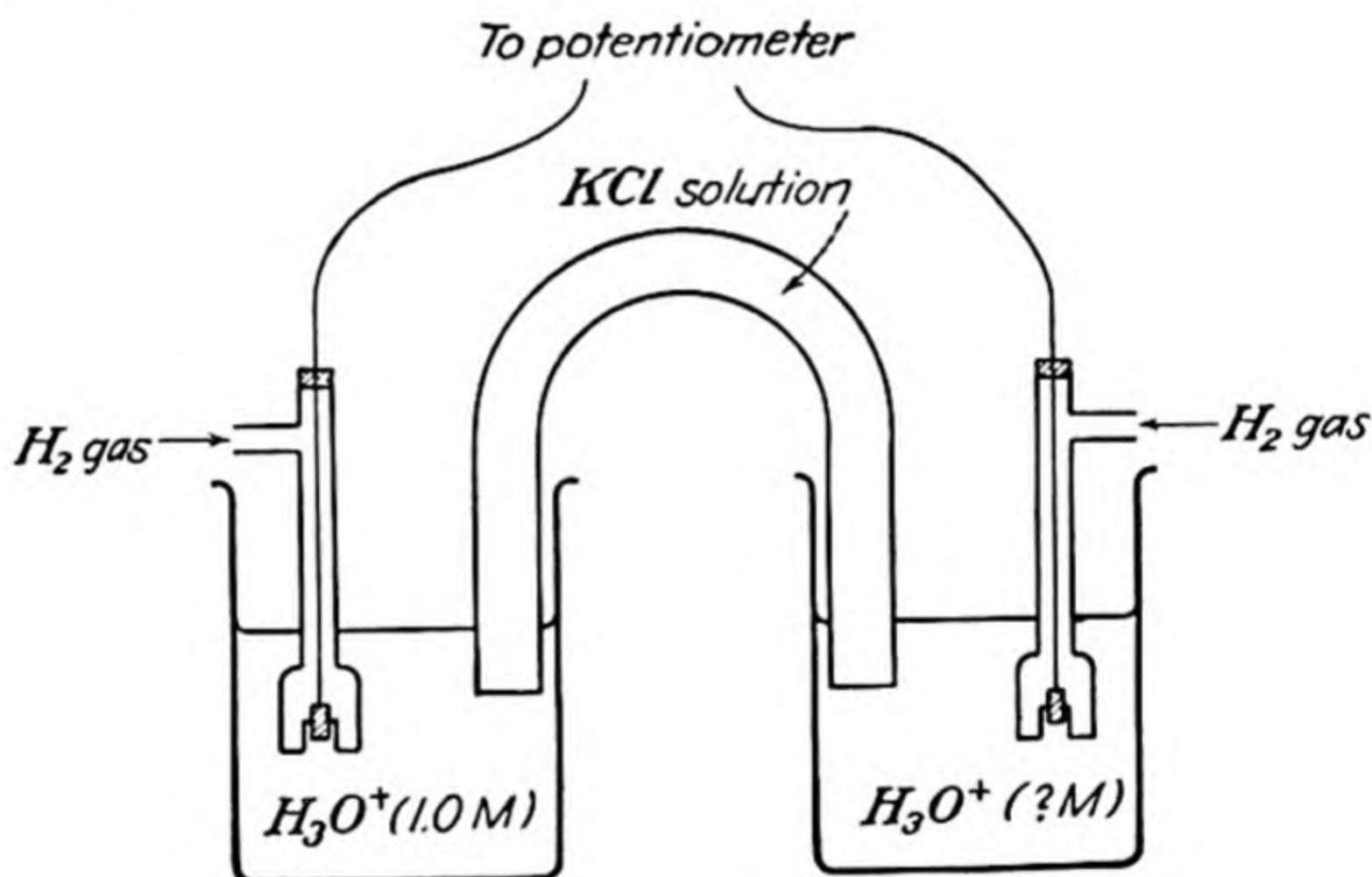
FIG. 9-2. A cell composed of two hydrogen electrodes.

The difference in potential between the two electrodes composing this cell can be measured by methods that will be discussed in succeeding sections. This difference in potential is always measured as the potential of the left-hand electrode minus the potential of the right-hand electrode.

$$E_{cell} = E_{left} - E_{right}$$

Therefore, if the cell potential is measured and if the potential of one of the electrodes is known, the potential of the other electrode can be calculated, and from this the concentration of hydronium ion around that electrode.

Just as in the case of electrode potentials, there are certain conventions that must be followed in dealing with cell potentials. These conventions are:

1. The cell potential is always equal to the electrode potential of the left-hand electrode minus that of the right-hand electrode.

2. The sign of the cell potential is always the same as the polarity of the right-hand electrode.

3. Electrons flow through the external circuit from the negative electrode to the positive electrode.

4. The electrode at which electrons leave the cell is called the anode; that at which they enter the cell is called the cathode.

5. Through the salt bridge, cations flow toward the cathode and anions flow toward the anode.

Example 1. Calculate the potential, at 25°C., of the following cell:

$$Pt + H_2 \text{ (1 atm.) } | \; H_3O^+ \text{ (3.0}m\text{) } | \; KCl \; | \; H_3O^+ \text{ (2.0}m\text{) } | \; H_2 \text{ (1 atm.) } + Pt$$
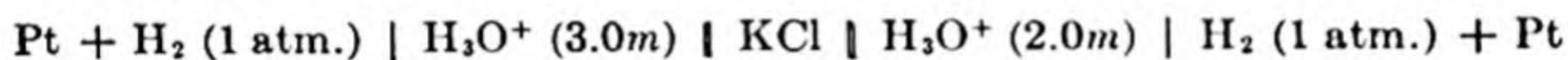
$$E_{cell} = E_{left} - E_{right}$$
$$E_{cell} = (-0.059 \log 3.0) - (-0.059 \log 2.0)$$
$$E_{cell} = (-0.059 \times 0.477) - (-0.059 \times 0.301)$$
$$E_{cell} = (-0.028) - (-0.018) = -0.010 \text{ volt}$$

The negative sign for the cell potential means that the right-hand electrode is the negative pole of the cell.

Example 2. The value of the cell potential, at 25°C., for the following cell

$$Pt + H_2 \text{ (1 atm.) } | \; H_3O^+ \text{ (1.0}m\text{) } | \; KCl \; | \; H_3O^+ \text{ (?}m\text{) } | \; H_2 \text{ (1 atm.) } + Pt$$
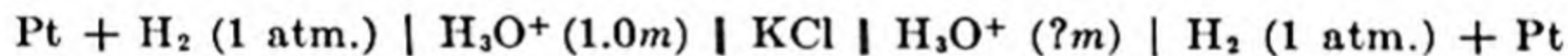
is 0.060 volt, the right-hand electrode being the positive pole. Calculate the concentration of hydronium ion around the right-hand electrode.

Note that the left-hand electrode is a normal hydrogen electrode for which $E = 0.000$ volt. Therefore

$$E_{cell} = E_{left} - E_{right}$$
$$E_{cell} = 0.000 - (-0.059 \log [H_3O^+])$$
$$+0.060 = +0.059 \log [H_3O^+]$$
$$\log [H_3O^+] = \frac{+0.060}{+0.059} = +1.02$$
$$[H_3O^+] = 10.5$$

The Calomel Electrode. While the normal hydrogen electrode is the ultimate standard for all potential measurements, it is difficult to prepare and to maintain. Therefore, it has been found more convenient in practice to use other, more easily prepared, standard electrodes. Chief among these is the *calomel electrode*.

The composition of the calomel electrode is indicated in Fig. 9-3.   Its conventional representation is

$$Hg + Hg_2Cl_2 \mid KCl$$
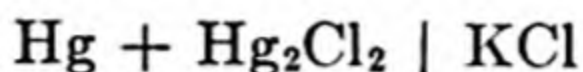
There are three types of calomel electrodes in common use. They are named according to the concentration of potassium chloride present in the electrode.

1. *The Decinormal Calomel Electrode.*   This is represented as

$$Hg + Hg_2Cl_2 \mid KCl\ (0.1N)$$
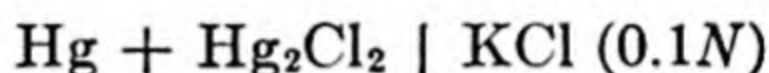
The potential of this electrode, at 25°C., is

$$E_{0.1N\ calomel} = -0.338 \text{ volt}$$

2. *The Normal Calomel Electrode.* This is represented as

$$Hg + Hg_2Cl_2 \mid KCl\ (1.0N)$$

Fig. 9-3.   A calomel electrode.
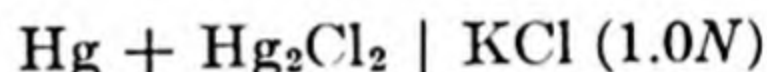
The potential of this electrode, at 25°C., is

$$E_{1.0N\ calomel} = -0.281 \text{ volt}$$

3. *The Saturated Calomel Electrode.*   This is represented as

$$Hg + Hg_2Cl_2 \mid KCl\ (satd.)$$
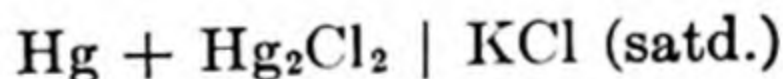
The potential of this electrode, at 25°C., is

$$E_{satd.\ calomel} = -0.246 \text{ volt}$$

The calomel electrode can be combined with a hydrogen electrode in the type of cell illustrated in Fig. 9-4 and represented as

$$Hg + Hg_2Cl_2 \mid KCl\ (0.1N) \mid H_3O^+\ (?m) \mid H_2\ (1\ atm.) + Pt$$
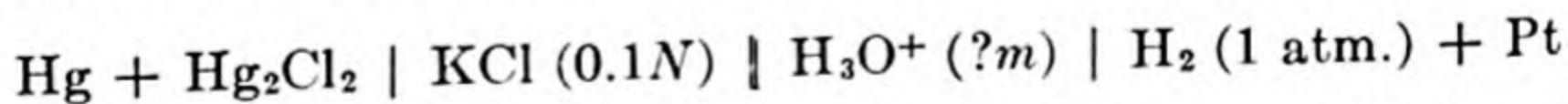
Example.   The value of the cell potential, at 25°C., of the following cell is −0.72 volt.   What is the concentration of hydronium ion in the cell?

$$Hg + Hg_2Cl_2 \mid KCl\ (satd.) \mid H_3O^+\ (?m) \mid H_2\ (1\ atm.) + Pt$$
$$E_{cell} = E_{left} - E_{right} = -0.246 + 0.059 \log [H_3O^+] = -0.72$$
$$\log [H_3O^+] = \frac{-0.72 + 0.246}{0.059} = -8.03 = \bar{9}.97$$
$$[H_3O^+] = 9.3 \times 10^{-9}$$
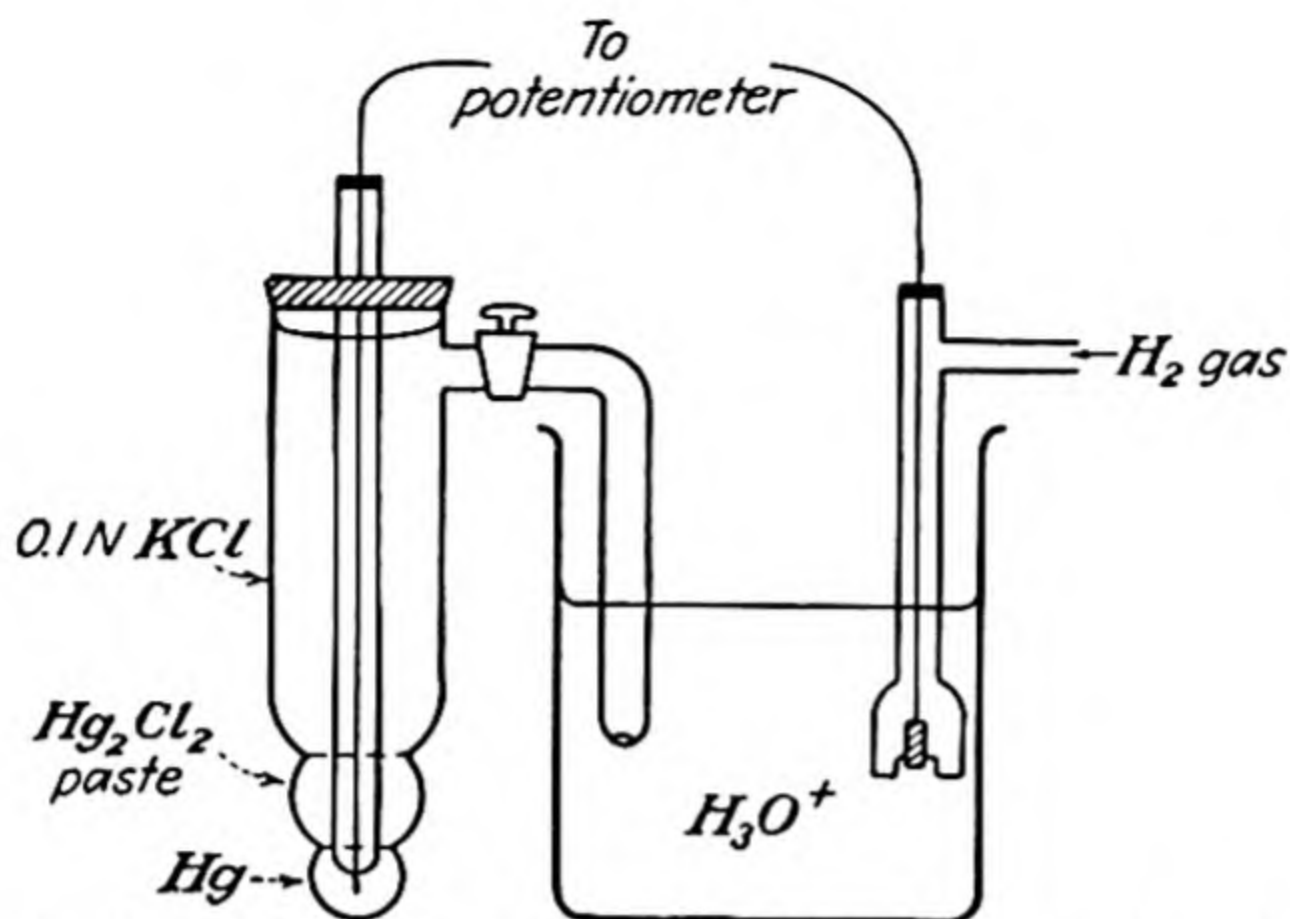
Fig. 9-4. A cell composed of a decinormal calomel electrode and a hydrogen electrode.

Other Electrodes

The Quinhydrone Electrode. It is at times inconvenient or impossible to use a hydrogen electrode for the determination of the concentration of hydronium ion. This is the case if the solution contains easily reducible substances, or if it contains dissolved gases, such as the carbon dioxide in blood, which would be swept out by the hydrogen, and whose removal would alter the pH of the solution being investigated. In many of these cases, the quinhydrone electrode, devised by Biilmann, has found a wide applicability.

Hydroquinone may be oxidized to quinone according to the reaction

$$\underset{\text{Hydroquinone}}{C_6H_4(OH)_2} + 2H_2O \rightleftharpoons \underset{\text{Quinone}}{C_6H_4O_2} + 2H_3O^+ + 2e$$
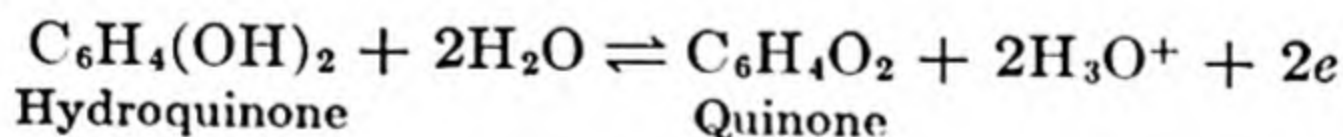
This is a reversible reaction in which electrons are released, and if an inert electrode is inserted into the solution, an electrode potential is developed whose value is given by the expression

$$E = E° - 2.303 \frac{RT}{nF} \log \frac{[C_6H_4O_2][H_3O^+]^2}{[C_6H_4(OH)_2]} \tag{9-13}$$

For this electrode at 25°C. we may, since $n = 2$, rewrite Eq. (9-13) to read

$$E = E° - \frac{0.059}{2} \log \frac{[C_6H_4O_2]}{[C_6H_4(OH)_2]} - \frac{0.059}{2} \log [H_3O^+]^2 \tag{9-14}$$

In the special case when the concentration of quinone is equal to that of hydroquinone, the second term on the right-hand side of Eq. (9-14) becomes equal to zero and the equation may be rewritten to read

$$E = E° - 0.059 \log [H_3O^+] \qquad (9\text{-}15)$$

Therefore, if we can arrange things so that the concentration of quinone shall be maintained equal to that of hydroquinone, this electrode can be used to measure the concentration of hydronium ion in a solution.

Fortunately it is easy to satisfy the condition that the concentration of quinone shall equal that of hydroquinone. This can be accomplished by using a solution of the slightly soluble substance, quinhydrone.

Quinhydrone may be represented as containing one molecule of hydroquinone and one molecule of quinone, corresponding to the formula $C_6H_4(OH)_2 \cdot C_6H_4O_2$. When this is placed in water solutions having a pH not greater than 8.0 it is largely converted into equal numbers of molecules of hydroquinone and quinone,

$$C_6H_4(OH)_2 \cdot C_6H_4O_2 \rightleftharpoons C_6H_4(OH)_2 + C_6H_4O_2$$
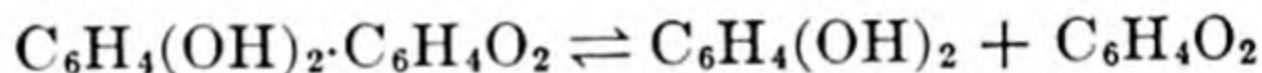
Accordingly, the use of a solution of quinhydrone does satisfy the condition that the concentration of quinone shall equal that of hydroquinone.

The value of the standard electrode potential for the quinhydrone electrode is

$$E° = -0.699 \text{ volt}$$

In writing conventional expressions for the quinhydrone electrode, we shall use the symbol QH to represent quinhydrone.

Example. The potential, at 25°C., of the following cell

$$\text{Pt} \mid \text{QH} + H_3O^+ \ (?m) \mid \text{KCl} \ (0.1N) \mid Hg_2Cl_2 + Hg$$
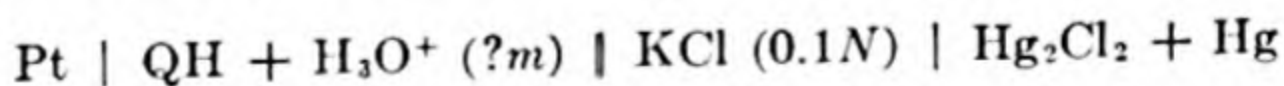
is 0.017 volt, the quinhydrone electrode being the negative pole. Calculate the pH of the solution around that electrode.

$$E_{cell} = E_{left} - E_{right}$$
$$+0.017 = (-0.699 - 0.059 \log [H_3O^+]) - (-0.338)$$
$$\text{pH} = -\log [H_3O^+] = \frac{+0.017 + 0.699 - 0.338}{0.059} = 6.4$$

Hydroquinone is not so easily oxidized as is hydrogen gas on platinum black. Therefore, the quinhydrone electrode may be used in some cases where the hydrogen electrode cannot be employed. It cannot be expected, however, to give good results in solutions whose pH is greater than 8.0. This is because in alkaline solutions hydroquinone is oxidized by contact with the oxygen of the air and, as a consequence, the value of the ratio of the concentration of quinone to that of hydroquinone is no longer equal to unity. For the same reason the quinhydrone electrode cannot be used for pH measurements in solutions having a large oxidizing or reducing potential and capacity.

The Glass Electrode. For use in solutions in which the hydrogen and quinhydrone electrodes are not practicable, the glass electrode has been devised. This consists of an extremely thin (0.001- to 0.025-mm.) glass membrane, enclosing an acid solution into which is inserted a suitable electrode.

A typical glass electrode might have the composition shown in Fig. 9-5 and represented conventionally as

$$\text{Pt} \mid \text{QH (satd.)} + \text{H}_3\text{O}^+ \mid \text{glass}$$
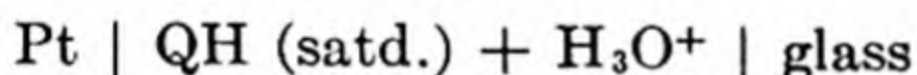
A variety of solutions and electrodes may be used inside the membrane.

Fig. 9-5. A glass electrode.

Although the functioning of the glass electrode is not completely understood, it is probably somewhat as follows. When this electrode is placed in contact with a solution whose pH is to be measured, the following electrode is established:

$$\text{Pt} \mid \text{QH (satd.)} + \text{H}_3\text{O}^+ \mid \text{glass} \mid \text{H}_3\text{O}^+ \,(?m)$$
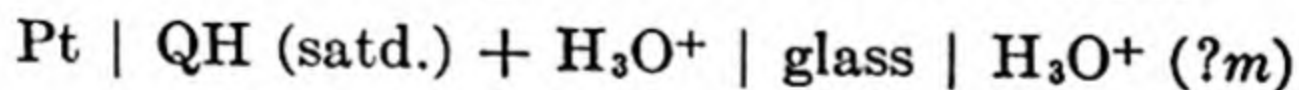
The glass acts as a membrane permitting the passage of hydronium ions from one solution to the other, but preventing the passage of other ions except at very high values of pH. Because the transfer of hydronium ions from one concentration to another involves a change in free energy, there is established across the glass membrane a potential, the value of which is determined by the difference in hydronium-ion concentration on the two sides of the membrane.

The total potential developed by the particular electrode that we are considering will be composed of three factors.

1. The potential for the quinhydrone electrode.

2. A potential depending on the chemical composition of the glass in the membrane. Proper selection of a glass can make the value of this potential very small.

3. The potential caused by the difference in concentration of hydronium ion on the two sides of the membrane.

The potential due to the first two factors will be a constant for any particular electrode and may be considered to be the standard electrode potential $E°$ for the electrode. The total potential of the electrode, at 25°C., will then be given by the expression

$$E = E° - 0.059 \log [H_3O^+] \tag{9-16}$$

The expression $[H_3O^+]$ appearing in Eq. (9-16) refers to the concentration of hydronium ion in the solution into which the glass electrode is inserted. The effect of the concentration of hydronium ion inside the membrane on the potential is included in the value of $E°$. Since the value of $E°$ depends on the chemical composition of the glass in the membrane and also on the nature of the electrode used inside the membrane, the value of this standard electrode potential must be determined experimentally for each electrode.

The experimental determination of the value of $E°$ for the electrode that we are considering can be made in the type of cell shown in Fig. 9-6 and represented conventionally as

Pt | QH (satd.) + H_3O^+ | glass | H_3O^+ (0.001m) | KCl (satd.) | Hg_2Cl_2 + Hg
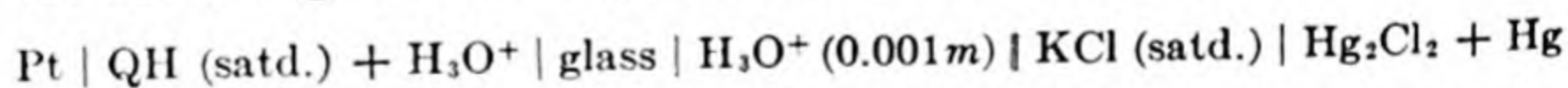
The measured potential of this cell, at 25°C., is 0.277 volt, the glass electrode being the positive pole.

$$E_{cell} = E_{left} - E_{right}$$
$$-0.277 = (E° - 0.059 \log [H_3O^+]) - (-0.246)$$
$$-0.277 = E° - 0.059 \log 0.001 + 0.246$$
$$-0.277 = E° + 0.177 + 0.246$$
$$E° = -0.277 - 0.177 - 0.246 = -0.700$$

Cells employing glass electrodes have been used successfully for the measurement of pH in the presence of such strong oxidizing agents as a permanganate solution. The electrode may be

used to measure the pH of very small quantities of solution. It will not contaminate the sample; hence the latter may be used for other determinations. The glass electrode thus possesses many advantages. There are, however, some limitations on its use. It gives good results in aqueous solutions whose pH lies between 1 and 9. In solutions whose pH is greater than 9 the electrode becomes less and less accurate as the pH increases, giving pH values that are lower than they should be until, for solutions whose pH is greater than 12, the results are not acceptable.
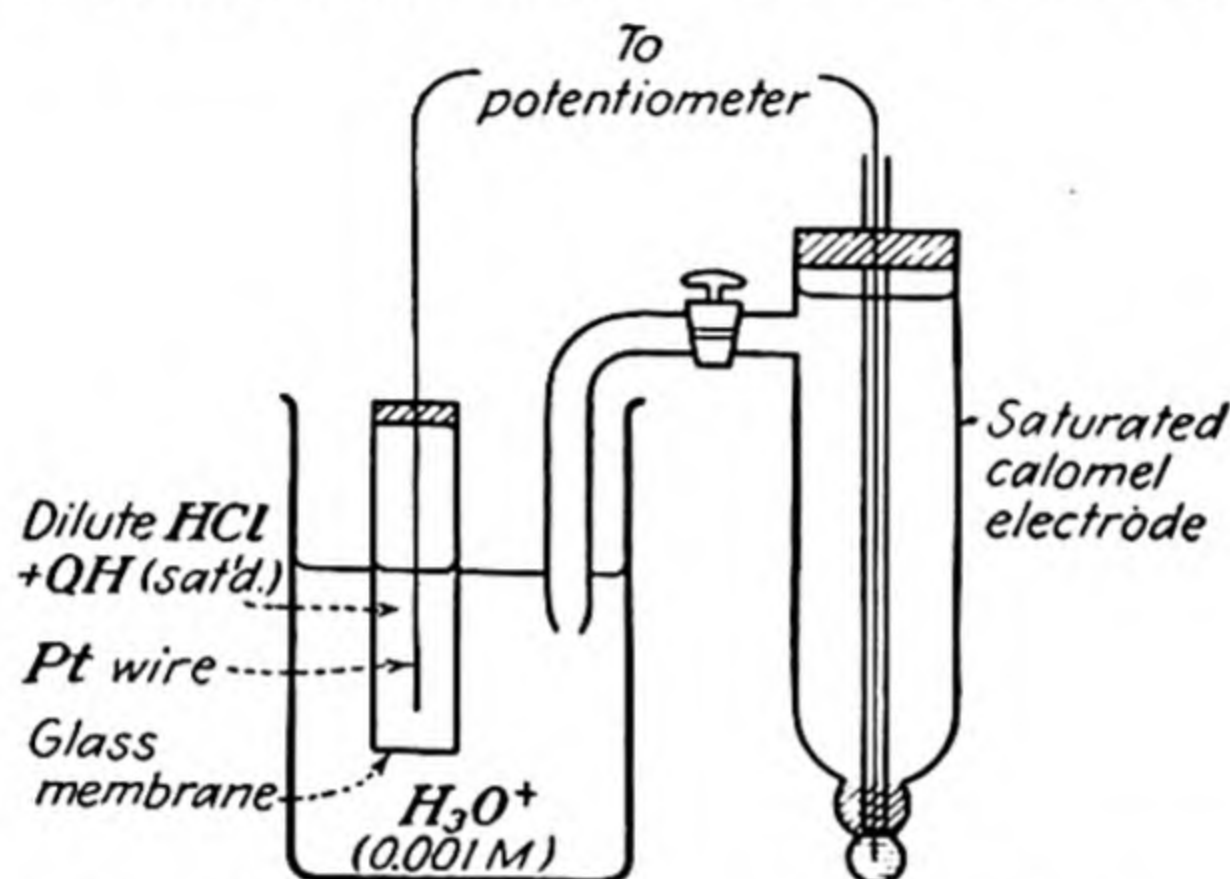
Fig. 9-6. Cell for pH measurement using the glass electrode.

The explanation advanced for this error is that in solutions of high pH the glass membrane permits the passage of ions of the alkali metals.

In very acid solutions the glass electrode gives pH values that are too high. The explanation advanced for this is that it is the hydronium ion (or hydrated proton) that passes through the glass membrane and anything that decreases the activity of water will affect the activity of the hydrated proton and, therefore, the potential corresponding to its passage through the glass. The addition of strong acids does decrease the activity of water. In confirmation of this theory is the fact that similar errors are observed when the activity of water is decreased by the addition of ethyl alcohol to a solution whose pH is maintained constant.

The resistance of the glass membrane is so large that only very minute currents are supplied by cells containing the glass elec-

trode.   Therefore, the circuit used to measure the potential must contain some amplifying device, such as radio-tube amplifiers.

The Measurement of Cell Potentials

The potential of a cell may be determined by comparing it with a standard cell whose voltage is known.   The standard cell which is commonly used has at one electrode cadmium amalgam in contact with a saturated solution of cadmium sulfate and at the other electrode mercury in contact with a saturated solution of mercurous sulfate.   This cell has a potential, at 20°C., equal to 1.0183 international volts, the cadmium amalgam being
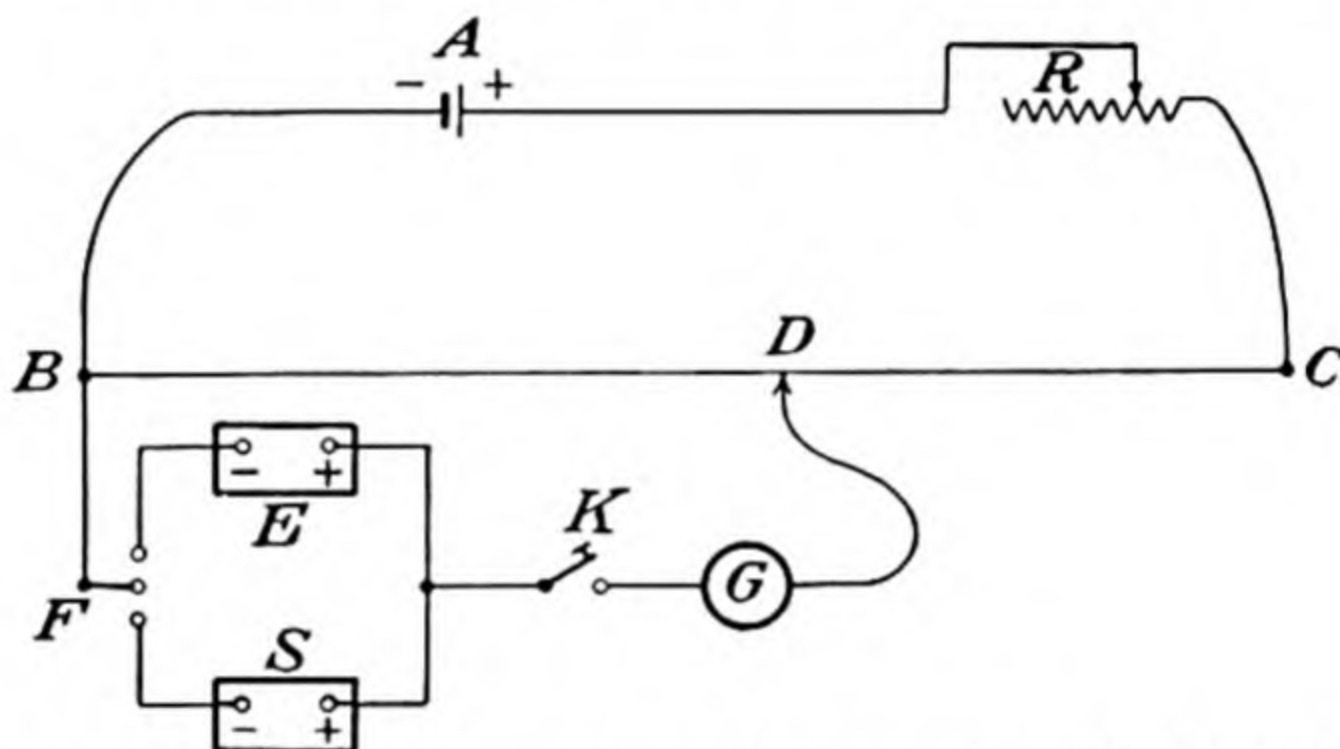
Fig. 9-7.   Potentiometer circuit for measuring cell potentials.

the negative pole.   The value of the potential varies only very slightly with changes of temperature and remains constant over long periods of time, thus making the cell a satisfactory standard with which to compare other cells.

The method by which comparison is made can best be explained by referring to the diagram of the potentiometer, Fig. 9-7.   In Fig. 9-7, A represents a storage cell providing a constant working potential of about 2.0 volts, BC represents a wire of uniform resistance, and R represents a variable resistance. S represents the standard cell, E the cell whose potential is to be measured, and F is a switch by which either cell can be put into the circuit. G is a galvanometer and D is a movable contact. K is a key for closing the circuit.

In making a determination, the switch F is closed, putting the standard cell into the circuit.   The contact D is moved until the distance BD is exactly 1,018.3 mm.   Then the resistance R is

varied until there is no deflection in the galvanometer G when the key K is tapped. Since no current flows through the galvanometer at this point, it means that the potential drop along the wire from B to D is the same as that through the standard cell, *viz.*, 1.0183 volts. Therefore, since the wire is of uniform resistance, we can say that each millimeter between B and C corresponds to a potential drop of 1 millivolt.

The switch F is now thrown to put the unknown cell E into the circuit, and the contact D is moved until once more there is no deflection in the galvanometer. The distance BD, measured in millimeters, now gives the potential of E in millivolts.

Note that in this circuit the cell is balanced against the working potential so that the slightest decrease in the latter will permit the cell reaction to go forward, the slightest increase will reverse the cell reaction. In other words, the cell reaction is being carried out reversibly. Under these conditions, the potential of the cell is a measure of the maximum useful work obtainable from the cell reaction and, therefore, of its decrease in free energy.

II. Indicator Methods

The electromotive-force methods are fundamental for the determination of hydronium-ion concentration and are always employed when the greatest accuracy is desired. For much routine physiological work, however, such accuracy is not necessary, and in these cases it is possible to employ other methods that are easier to use. Chief among these methods is that using indicators to show the concentration of hydronium ion.

Indicators

An indicator for measuring the concentration of hydronium ion is a weak organic acid or base whose protolysis is accompanied by a change in color. On the basis of the Brønsted system, an indicator may be defined as a conjugate acid-base system in which the acid and the base show different colors. The reasons why this color change occurs are beyond the scope of the present discussion. We shall concern ourselves only with the utilization of the process and not with its explanation.[1]

[1] For a discussion of the theory of the color change in indicators, see I. M. Kolthoff and C. Rosenblum, "Acid-Base Indicators," The Macmillan Company, New York, 1937.

We shall represent the protolysis of all acid-base indicators in aqueous solution as

$$\text{Acid form} + H_2O \rightleftharpoons H_3O^+ + \text{basic form}$$
$$\text{Color 1} \qquad\qquad\qquad\qquad \text{Color 2}$$
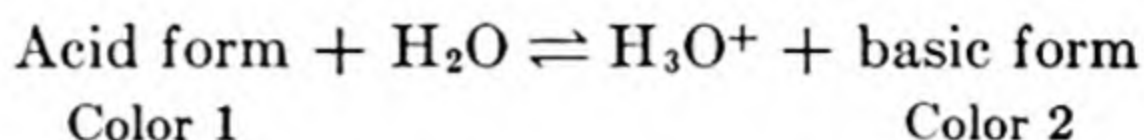
It is apparent from the above reaction that changes in the concentration of hydronium ion of the solution in which the indicator is placed will change the relative quantities of the acid and basic forms and so will change the color of the indicator.

The protolysis constant for the indicator reaction shown above is called the indicator constant for that indicator and is expressed as K_I.

$$K_I = \frac{[H_3O^+][\text{basic form}]}{[\text{acid form}]} \tag{9-17}$$

If we let x represent the fraction of the indicator in the basic form, then $(1 - x)$ represents the fraction in the acid form. Substituting these values in Eq. (9-17) gives

$$[H_3O^+] = K_I \frac{1 - x}{x} \tag{9-18}$$

or

$$\text{pH} = \text{p}K_I + \log \frac{x}{1 - x} \tag{9-19}$$

Table 9-2 lists several common indicators, giving their color changes, values of the indicator constant, and useful range.

TABLE 9-2. SOME COMMON INDICATORS

Indicator	Color		Approximate value of $\text{p}K_I$	Useful range pH
	Acid	Basic		
Thymol blue (acid range).	Red	Yellow	1.7	1.2 − 2.8
Methyl orange...........	Red	Orange	3.5	3.1 − 4.5
Bromphenol blue.........	Yellow	Purple	4.1	3.0 − 4.6
p-Nitrophenol...........	Colorless	Yellow	7.1	5.0 − 7.0
Bromthymol blue........	Yellow	Blue	7.3	6.0 − 7.6
Thymol blue (basic range)	Yellow	Blue	9.2	8.0 − 9.6
Phenolphthalein.........	Colorless	Red	(9.3)	8.0 − 9.8
Trinitrobenzene.........	Colorless	Brown	(13.5)	12.0 − 14.0

In Fig. 9-8 are plotted the values of x, the fraction of the indicator in the basic form, against values of pH for five of these indicators. The pH values were calculated for various values of x by using Eq. (9-19). In drawing these curves it is useful to note that when x is equal to 0.5 then pH is equal to pK_I. It will be noted that these curves all have the same shape but are displaced along the pH axis according to the value of pK_I for the indicator.
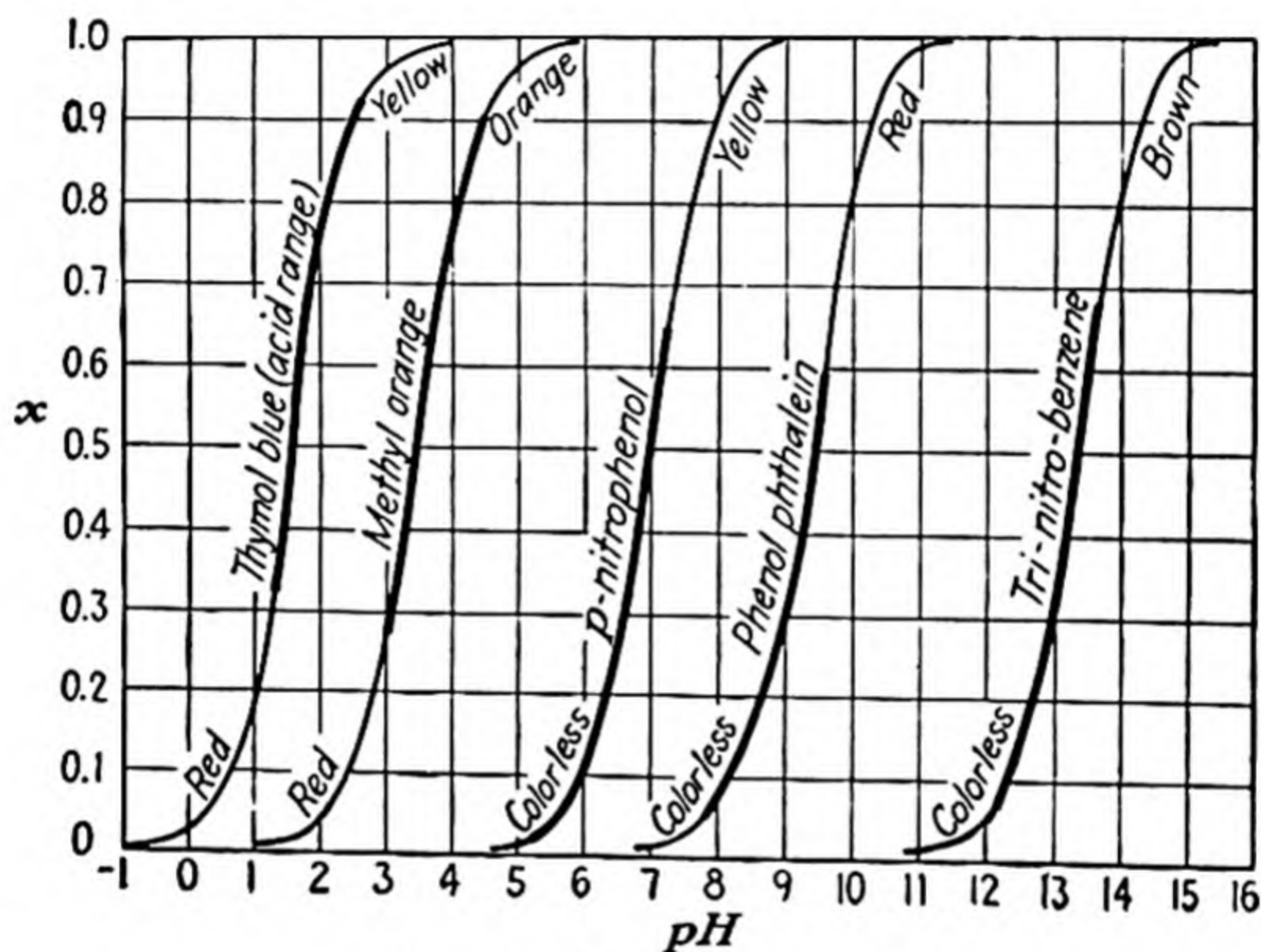
FIG. 9-8. Indicator curves.

The heavily shaded portion of each curve represents approximately the *useful range* of the indicator, *i.e.*, the interval between the first detectable color change and the point at which the transition is apparently complete. In general, this useful range extends from one pH unit below the value of pK_I to one pH unit above it. Examination of the curves, however, shows that the useful range does not cover the same interval for each indicator. If we compare methyl orange, which is a two-color indicator, with phenolphthalein, which is a one-color indicator, it is apparent that the first appearance of a pink color in a colorless solution of phenolphthalein should be easier to detect than the first appearance of an orange tinge in a red solution of methyl orange.

Accordingly, the useful range of phenolphthalein begins at a smaller value of x than does that of methyl orange. For two-color indicators the useful range depends somewhat on the relative tinctorial values of the two colors.

Approximate Determination of pH with Indicators

The pH of a solution can be shown to lie between certain limits by adding to separate samples of it a series of indicators with varying values of pK_I.* In this way it is found that with one indicator it gives the basic color, while with the indicator of next higher value of pK_I it gives the acid color. This will give the pH of the solution within two or three units.

For example, if distilled water has added to it a little phenolphthalein, the indicator remains colorless, showing that the pH of water is less than 8.0. On the other hand, if p-nitrophenol is added to water, the indicator is yellow, showing that the pH of water is greater than 6.0. The effect of solutions of different pH on the indicators in Fig. 9-8 is summarized in Table 9-3.

TABLE 9-3. COLOR CHANGES OF SOME INDICATORS

Solution	Indicator				
	Thymol blue	Methyl orange	p-Nitro-phenol	Phenol-phthalein	Trinitro-benzene
Sodium hydroxide.......	Blue	Orange	Yellow	Red	Brown
Ammonium hydroxide...	Blue	Orange	Yellow	Red	Colorless
Water...................	Yellow	Orange	Yellow	Colorless	Colorless
Sodium dihydrogen phosphate...............	Yellow	Orange	Colorless	Colorless	Colorless
Acetic acid.............	Yellow	Red	Colorless	Colorless	Colorless
Hydrochloric acid.......	Red	Red	Colorless	Colorless	Colorless

Various universal indicators have been devised. These are mixtures of several indicators having different values of pK_I so that the mixture shows several color changes covering a wide range of pH. A typical universal indicator may be prepared as follows. Take 100 mg. of phenolphthalein, 200 mg. of methyl red, 300 mg. of dimethylaminoazobenzene, 400 mg. of bromthy-

* The quantity of indicator added should, of course, be small enough so that it does not, of itself, change the pH of the solution appreciably.

mol blue, and 500 mg. of thymol blue. These are all dissolved in 500 ml. of 95 per cent ethyl alcohol, and enough $0.1N$ sodium hydroxide is added to produce a yellow color. This indicator shows the following colors:

pH	Color
2.0	Rose
4.0	Orange red
6.0	Yellow
8.0	Green
10.0	Blue

More Accurate Determinations of pH with Indicators

For more accurate determinations of pH, it is necessary to select an indicator such that the pH of the solution to be measured lies within the useful range of the indicator. When such an indicator has been found, it is possible to use it in either of two ways, either without a buffer or with a buffer.

Indicators without Buffers. It has been shown that throughout the useful range of an indicator the value of x, and also the color, changes very rapidly with changes in pH. If it were possible to translate shades of color into values of x for the indicator, these values of x could then be used in Eq. (9-19) to give the pH of the solution in which the indicator is used.

This translation of color into values of x is made possible by

FIG. 9-9. Cells using indicators without buffers.

the fact that the color of light transmitted by a solution containing 10 drops of an indicator which is 60 per cent in the basic form and 40 per cent in the acid form is the same as the color transmitted by a pair of solutions, one of which contains 4 drops of the indicator in the acid form and the other of which contains 6 drops of the indicator in the basic form. One way in which this

comparison can be made was devised by Gillespie[1] and is illustrated in Fig. 9-9. Cell A contains 4 drops of the indicator in 10 ml. of $0.001M$ hydrochloric acid. In the presence of this strong acid, the indicator may be considered as completely in the acid form. Cell B contains 6 drops of the indicator in 10 ml. of $0.001M$ sodium hydroxide. In the presence of the strong base, the indicator may be considered as completely in the basic form. Cell C contains 10 drops of the indicator in 10 ml. of the solution to be tested. Cell D contains 10 ml. of water and is used in order that the light shall be transmitted through the same depth of liquid in both cases. If the color seen through the cells A and B matches that seen through C and D, then it can be said that the value of x for the indicator in cell C is 0.6.

In practice, a series of the A and B cells are prepared with varying numbers of drops of the indicator in each, as follows:

	Number of drops of indicator						
Cell A (HCl).................	2	3	4	5	6	7	8
Cell B (NaOH)...............	8	7	6	5	4	3	2

The color seen through cells C and D is matched with one of the above pairs. Then x is proportional to the number of drops of indicator in cell B and $(1 - x)$ is proportional to the number of drops of indicator in cell A. These numbers may be substituted for x and $(1 - x)$ in Eq. (9-19) to give the pH of the solution in cell C.

It is not necessary that 10 drops of indicator be used in cell C, but it is necessary that the sum of the number of drops used in cells A and B be equal to the number used in C.

If the solution to be tested is itself colored, it is necessary, in order to compensate for this color, to add a third cell to each pair. Thus, to cells A and B is added a cell containing 10 ml. of the unknown solution without any indicator, and to cells C and D is added a cell containing 10 ml. of water.

Example. It is found that the color transmitted by an unknown solution containing 13 drops of bromcresol purple is matched by that transmitted through a pair of cells, containing in one cell 4 drops of the indicator in

[1] Gillespie, L. J., *J. Am. Chem. Soc.*, **42**, 742 (1920).

dilute sodium hydroxide and in the other cell 9 drops of the indicator in dilute hydrochloric acid. Calculate the pH of the solution.

The experimental results show that x is proportional to 4 and $(1 - x)$ is proportional to 9. Substitution of these values in Eq. (9-19) gives

$$pH = pK_I + \log \frac{x}{1 - x}$$
$$pH = 6.2 + \log \tfrac{4}{9}$$
$$pH = 6.2 - 0.352$$
$$pH = 5.8$$

The results of determinations of this type are probably reliable only to the first decimal place.
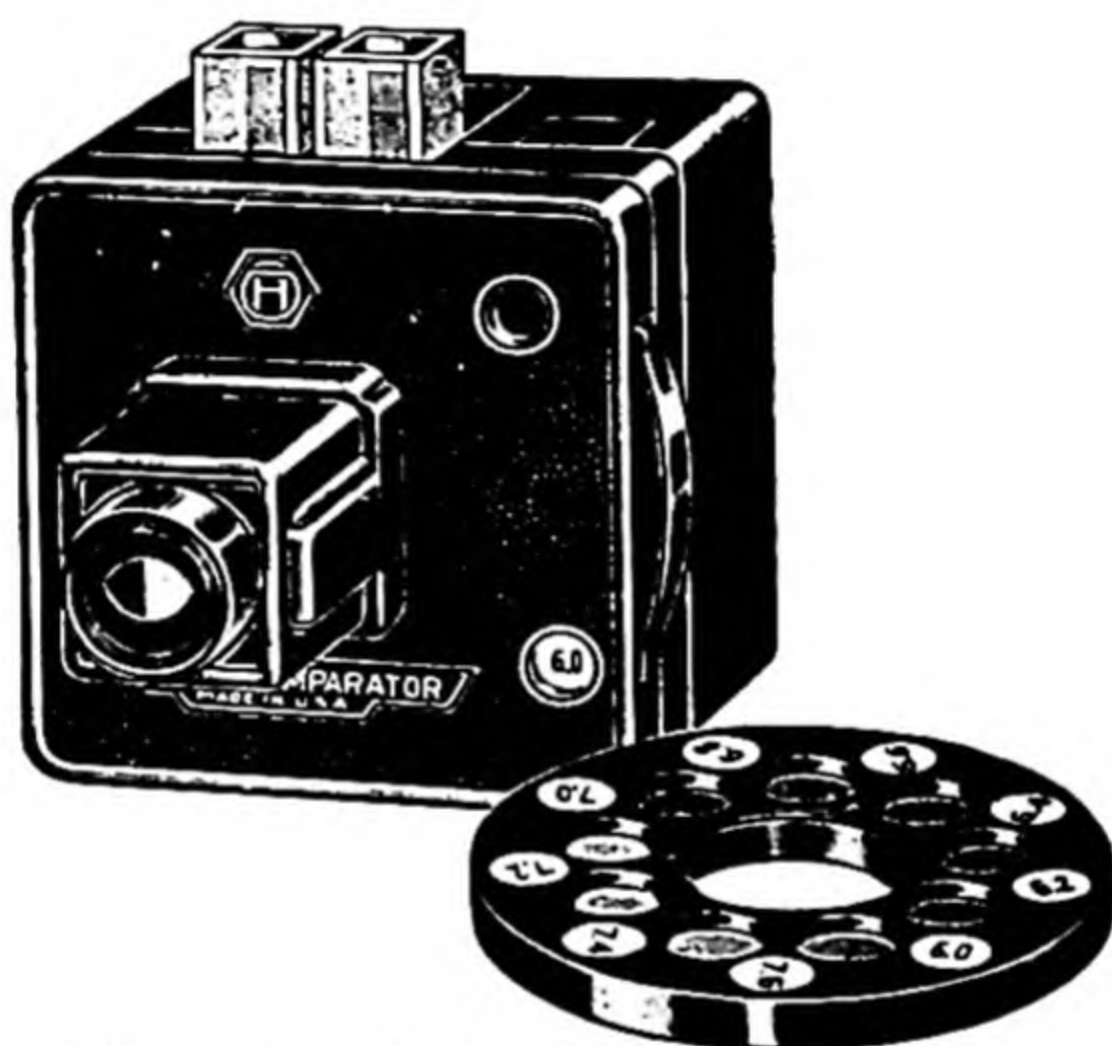
FIG. 9-10. The Hellige comparator for pH determinations. (*Courtesy of Hellige, Inc.*)

For many indicators there have been prepared sets of colored glass standards that correspond to the colors seen through the various combinations of A and B cells. The use of these standards simplifies the determination of pH. In the Hellige comparator, Fig. 9-10, these glass standards are mounted in a revolving disk so that the color seen through the unknown may be matched directly with that seen through the standard. The apparatus is so designed that the pH of the unknown can be read directly from the disk.

Indicators with Buffers. The second method for the determination of pH with indicators consists in preparing a series of standard buffer solutions, each having a known pH. These

solutions are so prepared that they cover the useful range of the indicator to be used, in steps of 0.1 or 0.2 of a pH unit. In Fig. 9-11a is shown a series of such standard solutions for use with the indicator phenolsulfonephthalein. Each tube contains the same volume of solution, and to each is added a fixed number of drops of the indicator. A series of color standards is thus provided throughout the useful range of the indicator.

In making a pH determination, the unknown solution and the indicator are added to a test tube in the same quantity as in the standards. The test tube is then placed in the middle space in a

| (a) Set of buffered standards. | (b) Comparator block. |
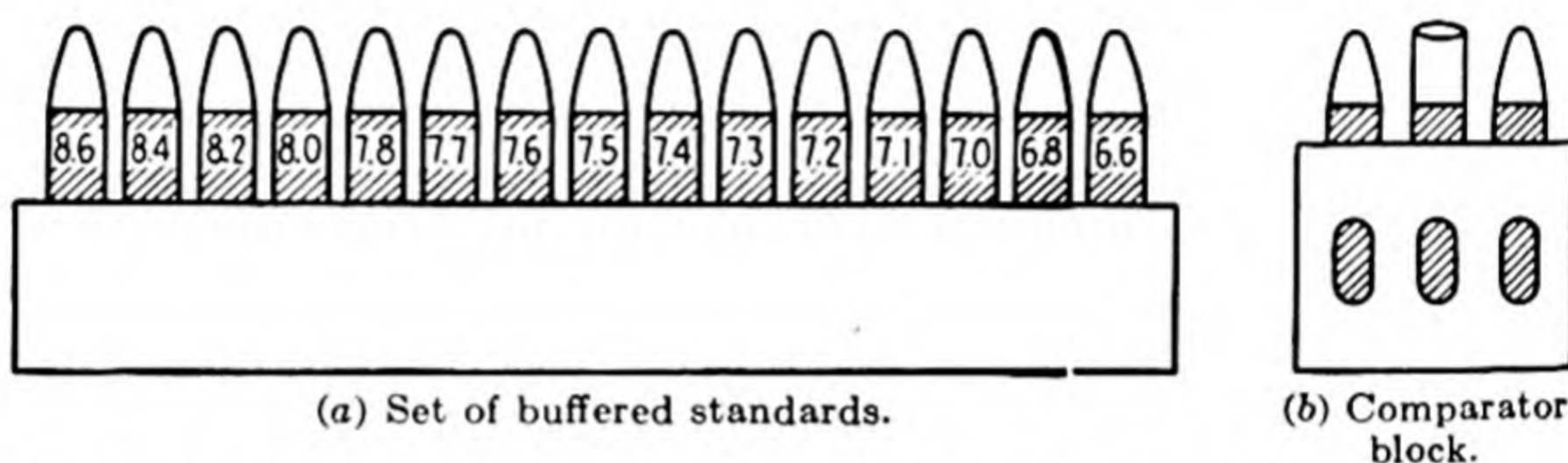
FIG. 9-11. Apparatus for determination of pH by means of indicator with buffers.

comparator block against a ground-glass background, Fig. 9-11b. On either side of the unknown are placed standards until it is found that the color of the unknown lies between the colors of two standards having adjacent pH values. Then it can be said that the pH of the unknown lies between those of the two standards used.

THE CONTROL OF THE CONCENTRATION OF HYDRONIUM ION

Buffer Solutions

A buffer solution is one whose pH is not altered to any great extent by the addition of considerable quantities of either hydronium ions or hydroxide ions. These buffer solutions are usually composed of a weak acid plus a salt of that acid, and it is this type that we shall consider. Other solutions which can show buffer action are those containing a weak base plus one of its salts, also solutions of ampholytes, and concentrated solutions of strong acids or strong bases.

The composition of a buffer containing a weak acid and one of its salts suggests that in this buffer the common ion effect is operative. Therefore, to calculate the pH of such a buffer we

may use Eq. (7-25).

$$\text{pH} = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]} \qquad (9\text{-}20)$$

Equation (9-20) is known as the Henderson-Hasselbalch equation for buffers.

By choosing an acid with a proper value of pK_a and by varying the proportions of acid and salt, it is possible to prepare buffer solutions of any desired pH. As an illustration of the method of calculating the pH of a buffer solution, and of the fact that the pH of a buffer solution changes less than that of an unbuffered solution upon the addition of the same amount of hydroxide ion, let us consider the following example.

Given two solutions of the following composition, calculate the pH of each solution.

1. $0.000018M$ hydrochloric acid.
2. A solution containing 0.1 mole of acetic acid and 0.1 mole of sodium acetate per liter.

For solution (1) we find

$$\text{pH} = -\log [H_3O^+] = -\log 1.8 \times 10^{-5} = 4.74$$

For solution (2) we find

$$\text{pH} = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]} = 4.74 + \log \frac{0.1}{0.1} = 4.74$$

Each of these solutions has the same pH, but the first one is not buffered, while the second one is buffered.

Now let there be added to 1 liter of each solution 0.000018 mole of sodium hydroxide. This is sufficient to neutralize the acid in the first solution, whose pH then becomes equal to 7.00. The effect of this addition of sodium hydroxide to the second solution, however, is to convert 0.000018 mole of acetic acid to sodium acetate, according to the reaction

$$HCH_3CO_2 + Na^+ + OH^- \rightleftharpoons H_2O + Na^+ + CH_3CO_2^-$$
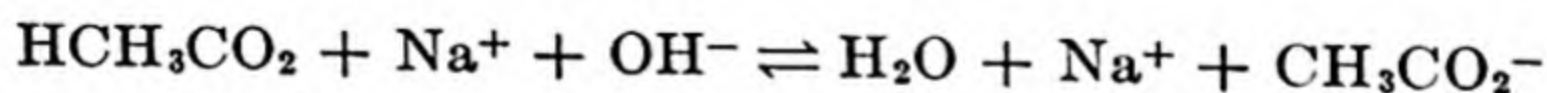
The pH of the buffer solution, following the addition of the sodium hydroxide, is

$$\text{pH} = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]} = 4.74 + \log \frac{0.1 + 0.000018}{0.1 - 0.000018} = 4.74$$

In other words, while the addition of this amount of hydroxide ion to the unbuffered solution causes its pH to increase by 2.26 units, the same amount of hydroxide ion changes the pH of the buffer by less than 0.01 unit.

A striking demonstration of this ability of buffers to absorb quantities of hydronium ions or hydroxide ions is afforded by the following experiment. Prepare the following solutions:

1. 100 g. of sodium dihydrogen phosphate in 500 ml. of water.
2. 100 g. of disodium hydrogen phosphate in 500 ml. of water.

Obtain four beakers, and label them *A*, *B*. *C*, and *D*. To these beakers, add the following mixtures:

Beaker *A*. 50 ml. of water + 5 drops of methyl orange.

Beaker *B*. 50 ml. of water + 5 drops of phenolphthalein.

Beaker *C*. 30 ml. of water + 10 ml. of solution (1) + 10 ml. of solution (2) + 5 drops of methyl orange.

Beaker *D*. 30 ml. of water + 10 ml. of solution (1) + 10 ml. of solution (2) + 5 drops of phenolphthalein.

The pH of each of these solutions is approximately 7.0. The contents of beakers *A* and *B* are unbuffered; the solutions in beakers *C* and *D* are buffered.

To beaker *A*, add 2 drops of 0.5*N* hydrochloric acid. This will cause the indicator to show its acid color. To beaker *B*, add 2 drops of 0.5*N* sodium hydroxide. This will cause the indicator to show its basic color. Now add 0.5*N* hydrochloric acid to beaker *C* until its color matches that in beaker *A*. This will require several milliliters of the acid. Add 0.5*N* sodium hydroxide to beaker *D* until its color matches that in beaker *B*. This will require several milliliters of the base.

The Efficiency of Buffers. In Fig. 9-12 are plotted the values of pH obtained from Eq. (9-20) for different values of the ratio [salt]/[acid] for the buffer solution containing acetic acid and sodium acetate. In order to conserve space, the ordinates below the dotted line are for the ratio [salt]/[acid], while above the dotted line they are for the ratio [acid]/[salt]. The dotted line passes through the point where the concentration of the acid is equal to that of the salt, and hence the value of either of the above-mentioned ratios is equal to 1.0. At this point, according to Eq. (9-20), the pH of the buffer is equal to pK_a.

It will be noted that the curve in Fig. 9-12 is steepest in the neighborhood of the dotted line. In this region it is possible to have the greatest change in the value of the ratio [salt]/[acid] (*i.e.*, to move the greatest distance up or down the curve) with the smallest corresponding change in the pH of the solution. In other words, when the concentration of the salt is equal to that of the acid, the buffer is most efficient. At this point it is possible to add the greatest quantity of hydronium ions or hydroxide ions with the least change in the pH of the solution. On either side of this point, the buffer becomes decreasingly efficient as the curve flattens out.
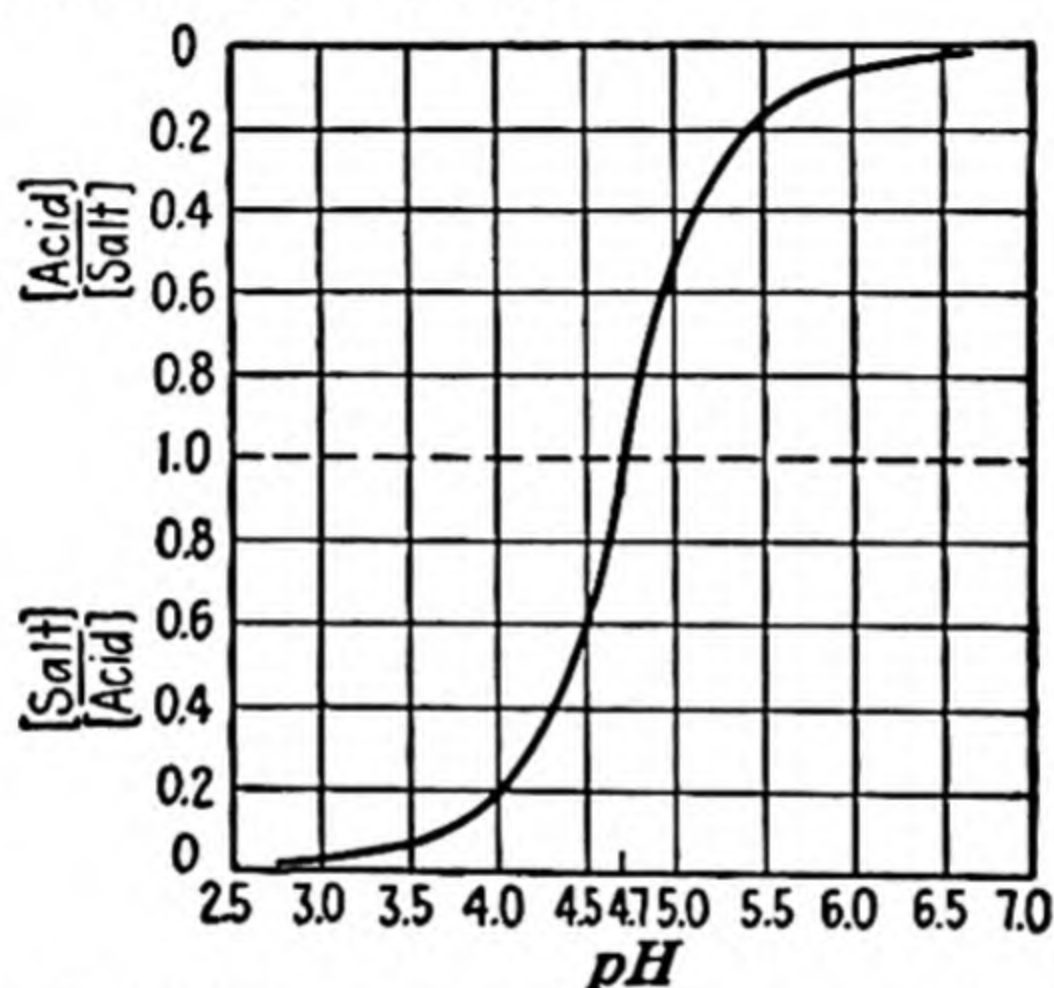
Fig. 9-12. The pH curve for buffer containing acetic acid and sodium acetate.

The efficiency of the buffer is inversely proportional to the magnitude of the expression log [salt]/[acid] without regard to sign. When the value of this expression is zero, the buffer is at its most efficient point.

As an illustration of this change in efficiency, let us consider the following example. To 1 liter of a buffer, containing 0.10 mole of acetic acid and 0.10 mole of sodium acetate, hydrogen chloride is added in increments of 0.01 mole at a time. Calculate the change in pH resulting from each addition of hydrogen chloride.

Before any hydrogen chloride is added, the pH of the buffer is

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]} = 4.74 + \log \frac{0.10}{0.10} = 4.74$$

At this point the buffer is working at its maximum efficiency. Each addition of hydrogen chloride will convert 0.01 mole of sodium acetate into acetic acid according to the reaction

$$Na^+ + CH_3CO_2^- + H_3O^+ + Cl^- \rightleftharpoons Na^+ + HCH_3CO_2 + H_2O + Cl^-$$
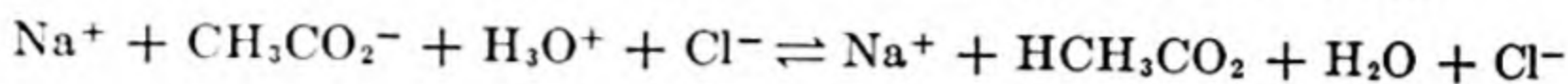
Therefore, following the addition of the first increment of hydrogen chloride, the pH is

$$pH = 4.74 + \log \frac{0.10 - 0.01}{0.10 + 0.01} = 4.65$$

Following the addition of the eighth increment, the pH is

$$pH = 4.74 + \log \frac{0.10 - 0.08}{0.10 + 0.08} = 3.79$$

and following the addition of the ninth increment, the pH is

$$pH = 4.74 + \log \frac{0.10 - 0.09}{0.10 + 0.09} = 3.46$$

The addition of the first increment of 0.01 mole of hydrogen chloride produced a decrease in pH of 0.09 unit, while the addition of the ninth increment produced a decrease of 0.33 unit, showing that the efficiency of the buffer had decreased greatly.

We have seen that the efficiency of a buffer increases as the value of log [salt]/[acid] approaches zero. For any given value of this logarithm, the efficiency of the buffer also increases as the concentrations of the salt and acid increase.

Consider a buffer containing 1.00 mole of acetic acid and 1.00 mole of sodium acetate per liter. The pH of this buffer is .

$$pH = 4.74 + \log \frac{1.00}{1.00} = 4.74$$

To 1 liter of this buffer is added 0.01 mole of hydrogen chloride. Following this addition of acid, the pH is

$$pH = 4.74 + \log \frac{1.00 - 0.01}{1.00 + 0.01} = 4.74$$

In this case the addition of 0.01 mole of hydrogen chloride per liter of buffer changes the pH by less than 0.01 unit. Contrast this with the case in which the addition of the same amount of hydrogen chloride to a buffer containing 0.10 mole of acetic

acid and 0.10 mole of sodium acetate per liter caused a change in pH of 0.09 unit.

Thus we see that the efficiency of a buffer is determined by two factors: (1) the value of the expression log [salt]/[acid], and (2) the individual values of the concentrations of acid and salt. As a means of expressing the efficiency, or capacity, of a buffer Van Slyke has proposed the following expression:

$$\text{Buffer capacity} = \frac{d\text{B}}{d\text{pH}} \qquad (9\text{-}21)$$

In Eq. (9-21), dB represents the number of gram-equivalents of strong base added per liter of buffer, and dpH represents the

TABLE 9-4. CHANGES PRODUCED IN THE pH OF A BUFFER BY THE ADDITION OF A BASE

Total gram-equivalents of sodium hydroxide added	ΔB	pH	ΔpH
0.00		4.74	
	0.01		0.09
0.01		4.83	
	0.01		0.09
0.02		4.92	
	0.01		0.09
0.03		5.01	
	0.01		0.10
0.04		5.11	
	0.01		0.11
0.05		5.22	
	0.01		0.12
0.06		5.34	
	0.01		0.15
0.07		5.49	
	0.01		0.20
0.08		5.69	
	0.01		0.33
0.09		6.02	

resulting change in the pH of the buffer. This same equation may be used to express the effect of the addition of a strong acid to the buffer. The addition of acid is equivalent to the removal of base, *i.e.*, dB would be negative. Since this results in a

decrease in pH, the sign of dpH is also negative and, therefore, the sign of the buffer capacity is always positive.

Table 9-4 shows the changes in pH produced by the addition of successive increments of 0.01 gram-equivalent of sodium hydroxide to 1 liter of a buffer containing 0.10 mole of acetic acid and 0.10 mole of sodium acetate. These data are plotted in Fig. 9-13.

Since the buffer capacity is changing continuously as base is added, we find that for the addition of a finite quantity of base the
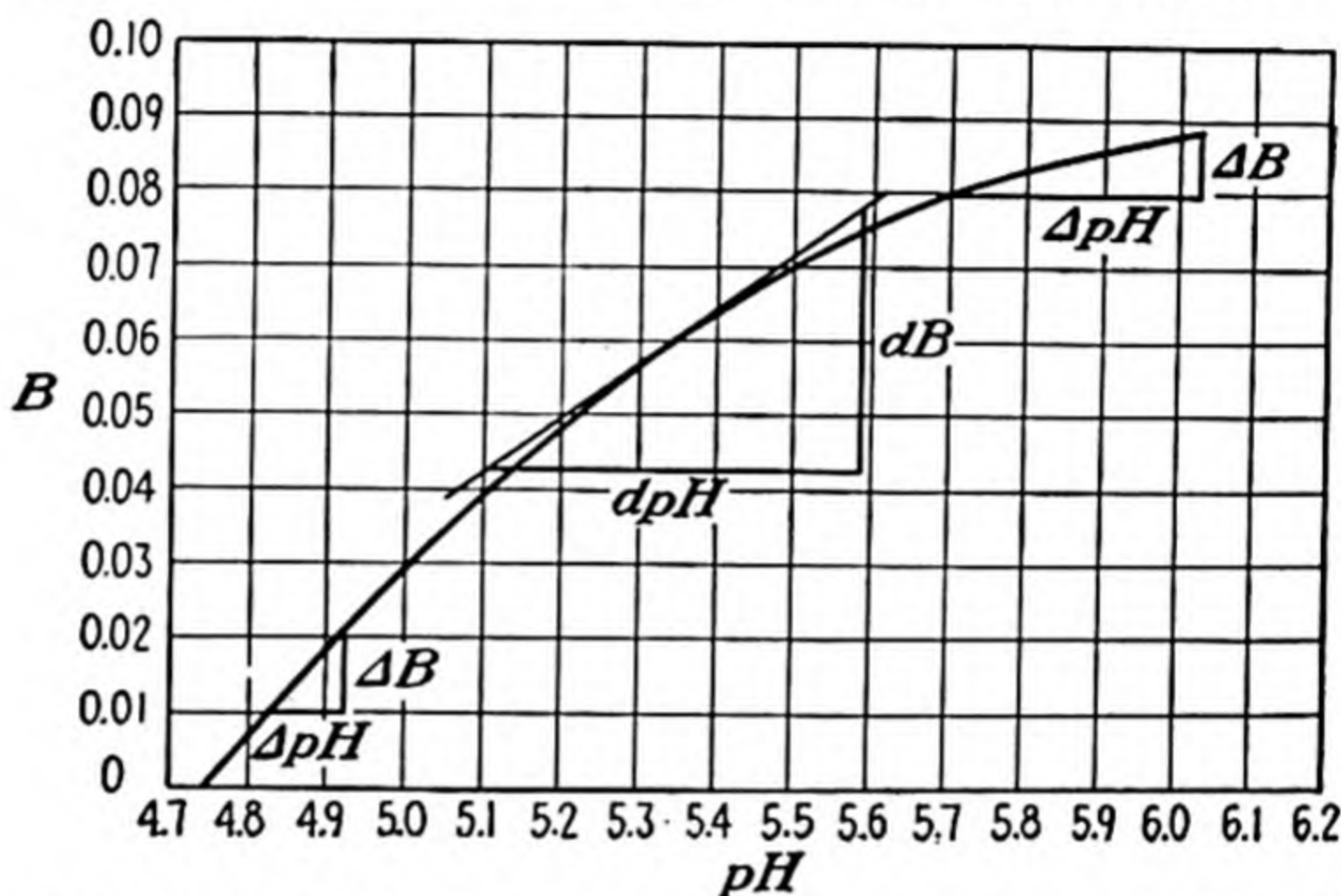
FIG. 9-13. Changes in pH caused by the addition of sodium hydroxide to a buffer containing 0.1 mole of acetic acid and 0.1 mole of sodium acetate per liter. B represents the gram-equivalents of base added per liter of buffer.

expression $\Delta B/\Delta$pH represents the *average buffer capacity* of the buffer during the interval in question. Thus, from Fig. 9-13, we find that the average capacity of the buffer for the pH interval from 4.83 to 4.92 is

$$\frac{\Delta B}{\Delta pH} = \frac{0.01}{0.09} = 0.11$$

Similarly, for the pH interval from 5.69 to 6.02, the average buffer capacity is

$$\frac{\Delta B}{\Delta pH} = \frac{0.01}{0.33} = 0.03$$

The expression dB/dpH represents the buffer capacity at any particular point along the curve and corresponds to the change in pH produced by the addition of an infinitesimal quantity of base. The buffer capacity at any point on the curve is equal to the slope

of the tangent to the curve at that point. The slope of the tangent is given by the expression

$$\frac{d\text{B}}{d\text{pH}} = 2.3 \frac{(\text{S} + \text{B})(\text{A} - \text{B})}{(\text{S} + \text{A})} \qquad (9\text{-}22)$$

In Eq. (9-22), S represents the original concentration of salt in the buffer, A represents the original concentration of acid in the buffer, and B represents the gram-equivalents of base that have been added per liter of buffer to reach the point in question.

Those familiar with the calculus can derive Eq. (9-22) by differentiating, with respect to pH, the following expression, which is the equation for the curve in Fig. 9-13:

$$\text{pH} = p K_a + \log \frac{(\text{S} + \text{B})}{(\text{A} - \text{B})}$$

Example 1.   What is the buffer capacity of a buffer containing 0.10 mole of formic acid and 0.20 mole of sodium formate per liter? A = 0.10, S = 0.20, and B = 0.0.

$$\frac{d\text{B}}{d\text{pH}} = 2.3 \times \frac{0.20 \times 0.10}{0.20 + 0.10} = 2.3 \times \frac{0.020}{0.30} = 0.15$$

Example 2.   What is the buffer capacity of the buffer in Example 1 after the addition of 0.02 mole of sodium hydroxide to one liter of the buffer? B = +0.02.

$$\frac{d\text{B}}{d\text{pH}} = 2.3 \times \frac{0.22 \times 0.08}{0.20 + 0.10} = 2.3 \times \frac{0.018}{0.30} = 0.14$$

Example 3.   What is the buffer capacity of the buffer in Example 1 following the addition of 0.03 mole of hydrochloric acid to one liter of the buffer? B = −0.03.

$$\frac{d\text{B}}{d\text{pH}} = 2.3 \times \frac{0.17 \times 0.13}{0.20 + 0.10} = 2.3 \times \frac{0.022}{0.30} = 0.17$$

The buffer capacity of a solution containing more than one buffer is equal to the sum of the capacities of the component buffers.

Buffers in the Blood. The pH of normal human blood is found to remain remarkably constant at about 7.35, which is slightly on the alkaline side of neutrality. Any marked deviations from this value are an indication of pathological conditions. For example, in diabetic coma the pH of the blood may drop to 6.82.

In order to maintain this constant pH which is necessary to health, the blood must contain a mechanism that is capable of handling the acids produced by the processes of digestion. Chief among these agencies are the buffers found in the blood stream. One of the buffers so found consists of carbonic acid and bicarbonate ion. Another buffer contains a mixture of monohydrogen phosphate ion and dihydrogen phosphate ion.

In the case of the buffer consisting of carbonic acid and bicarbonate ion, any increase in the concentration of hydronium ion in the blood causes the reaction

$$H_3O^+ + HCO_3^- \rightleftharpoons H_2CO_3 + H_2O$$
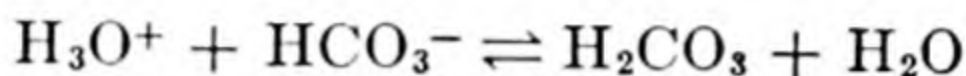
to go forward. The carbonic acid so formed decomposes into water and carbon dioxide. At the same time, the decrease in the pH of the blood stimulates the respiratory centers and causes deeper breathing, resulting in the elimination of the excess carbon dioxide through the lungs.

An increase in the concentration of hydroxide ion in the blood is absorbed by the reaction

$$H_2CO_3 + OH^- \rightleftharpoons HCO_3^- + H_2O$$
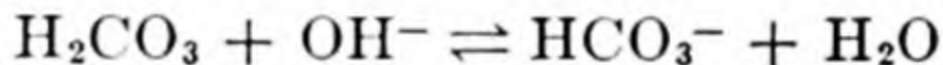
In Fig. 9-14 the curve for the buffer containing carbonic acid and bicarbonate ion is plotted from the equation

$$pH = pK_1 + \log \frac{[HCO_3^-]}{[H_2CO_3]}$$

in which $pK_1 = 6.31$ (at 38°C., blood temperature).

It will be noted that this buffer is working at its maximum efficiency at a pH of 6.31, but the pH of the blood is 7.35, which is considerably on the alkaline side of the point of maximum efficiency of the buffer (see point x on the curve). This circumstance, however, may be fortunate, for it is found that the majority of deviations from the normal pH are in the direction of increasing acidity, *i.e.*, decreasing pH. Examination of the curve shows that as the pH is decreased the buffer becomes more and more efficient in combating the excess hydronium ion that is being supplied to the blood.

In cases of severe hemorrhage, there is a decrease in the buffering power of the blood with an attendant rise in hydronium-

ion concentration. To combat this condition, bicarbonates are injected as in Locke's physiological salt solution.

According to Findlay, the efficiency of the buffers in the blood may be demonstrated by the fact that forty to seventy times as much sodium hydroxide must be added to blood serum as to water in order to give a normal red coloration with phenolphthalein, and more than three hundred times as much hydrochloric acid must be added to serum as to water in order to give a normal coloration with methyl orange.
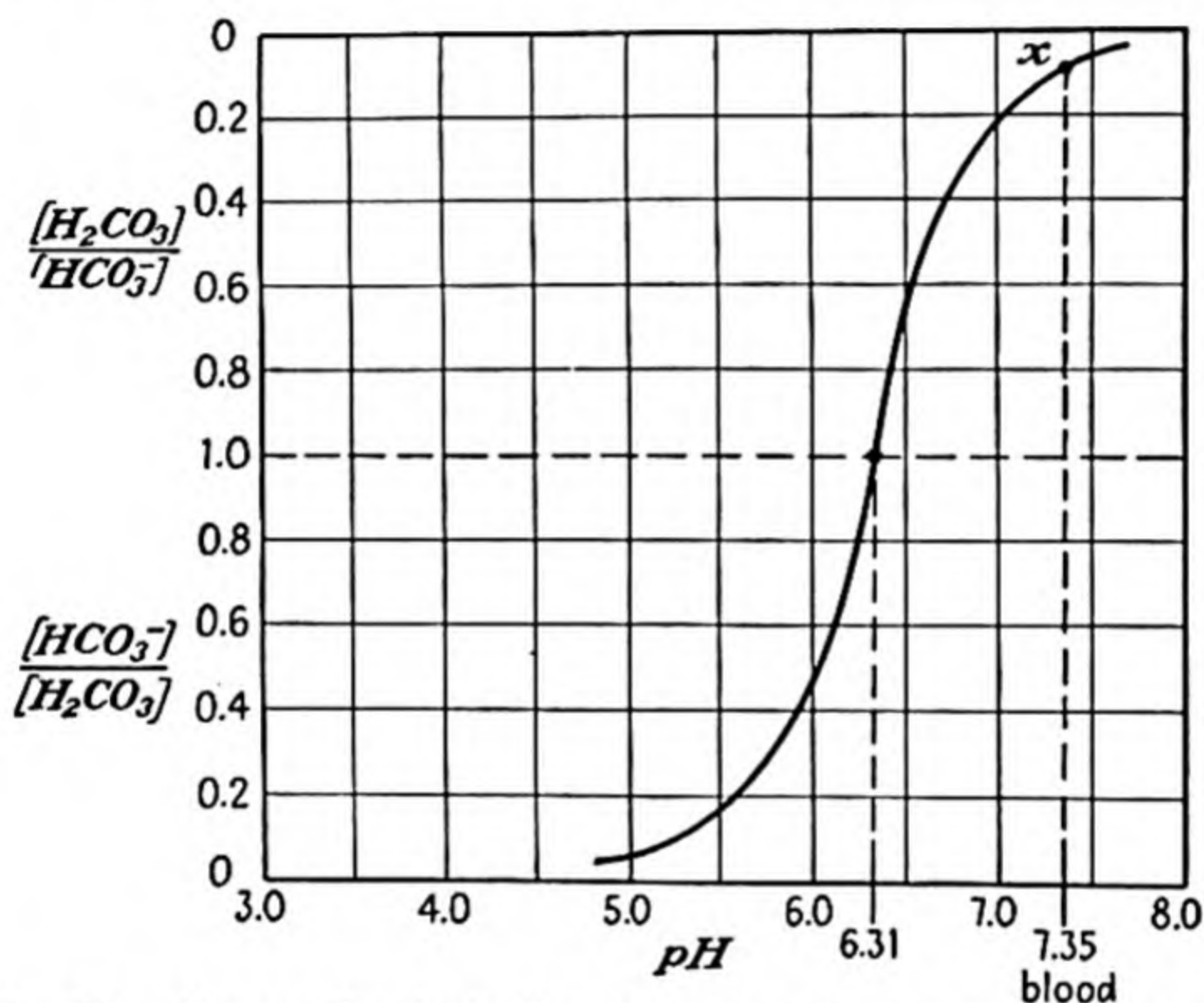
FIG. 9-14. The pH curve for the buffer containing carbonic acid and bicarbonate ion.

Other Agencies for Regulating the pH of the Blood. In addition to the buffer mixtures, there are also present in the blood various amphoteric substances that are capable of combining with excess hydronium ions or hydroxide ions and thus help to maintain the pH of the blood at its normal value.

The kidneys also help to maintain a constant concentration of hydronium ion in the blood by secreting more or less acid as the condition of the blood demands. Thus the pH of urine may vary over a wide range from 7.0 to 4.8.

The stomach contents are strongly acid, the pH of gastric juice lying between 2.0 and 1.4, so that vomiting is accompanied

by a decrease in the hydronium-ion concentration of the blood. On the other hand, the pancreatic juice and bile give an alkaline reaction to the intestinal contents so that diarrhea is accompanied by an increase in the hydronium-ion concentration of the blood and tissue fluids.

Control of the pH of various parts of the digestive tract is important because of the fact that the different digestive enzymes have definite pH values at which they are most efficient. Deviations from these pH values hinder or even stop the action of the enzyme. For example, pepsin acts in the stomach but not in the intestines, while trypsin is effective in the intestines but not in the stomach.

Problems

1. Calculate the potential, at 15°C., of the following electrode:

$$Pt + H_2 \ (2.0 \ atm.) \ | \ H_3O^+ \ (0.50m)$$

2. The potential, at 25°C., of the following electrode

$$Pt + H_2 \ (0.50 \ atm.) \ | \ H_3O^+ \ (?m)$$
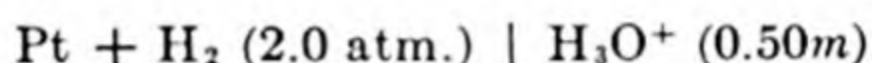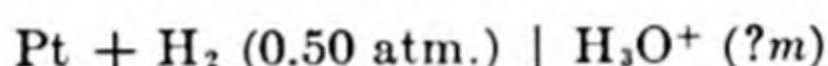
is +0.25 volt. What is the concentration of hydronium ion in the solution?

3. What is the potential, at 25°C., of an electrode consisting of hydrogen gas, at 1 atm., in contact with pure water?

4. Calculate the potential, at 20°C., of the following electrode:

$$Cu° \ | \ Cu^{++} \ (0.015m)$$
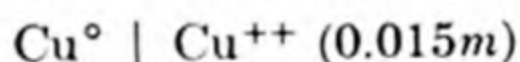
5. From the data in Table 9-1 calculate the standard free energy of formation of stannous ion.

6. From the data in Table 9-1 calculate the value of the equilibrium constant for the reaction $Ag° \rightleftharpoons Ag^+ + e$.

7. Calculate the potential, at 25°C., of the following cell. Which electrode is the positive pole?

$$Pt + H_2 \ (1 \ atm.) \ | \ H_3O^+ \ (0.15m) \ \| \ KCl \ \| \ H_3O^+ \ (2.5m) \ | \ H_2 \ (1 \ atm.) + Pt$$

8. The potential, at 25°C., of the following cell

$$Pt + H_2 \ (1 \ atm.) \ | \ H_3O^+ \ (1.0m) \ \| \ KCl \ \| \ H_3O^+ \ (?m) \ | \ H_2 \ (1 \ atm.) + Pt$$
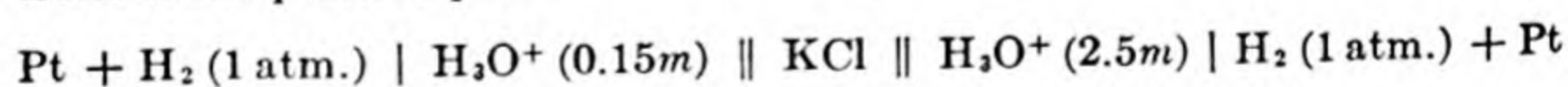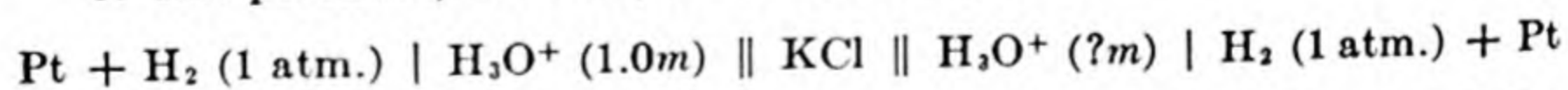
is +0.047 volt. What is the concentration of hydronium ion around the right-hand electrode?

9. Calculate the potential, at 25°C., of the following cell:

$$Zn° \ | \ Zn^{++} \ (0.01m) \ \| \ KCl \ \| \ Cl^- \ (0.003m) \ | \ Cl_2 \ (1 \ atm.) + C$$
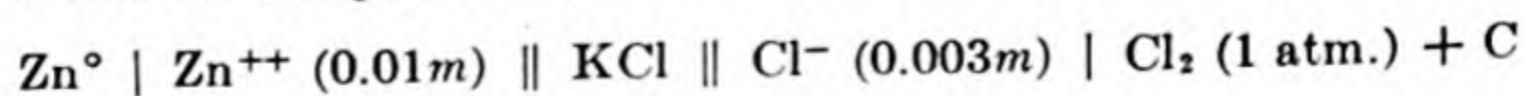
10. The potential, at 25°C., of the following cell

$$Zn° \ | \ Zn^{++} \ (1.0m) \ \| \ KNO_3 \ \| \ Ag^+ \ (?m) \ | \ Ag°$$
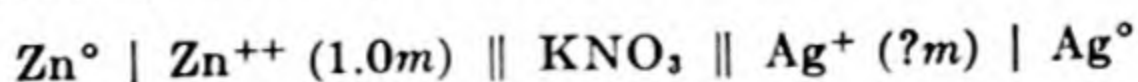
is $+1.50$ volts. What is the concentration of silver ion around the right-hand electrode?

11. Calculate the potential, at 25°C., of the following cell:

$$Hg + Hg_2Cl_2 \mid KCl \ (0.1N) \parallel H_3O^+ \ (0.02m) \mid H_2 \ (1 \text{ atm.}) + Pt$$
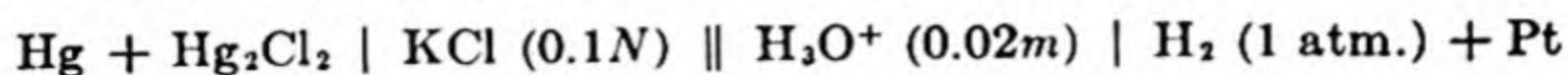
12. A cell is formed in which one electrode consists of hydrogen gas, at 1 atm., in contact with a solution whose pH $= 3.7$. The other electrode is a saturated calomel electrode. What is the potential, at 25°C., of the cell, and which electrode is the positive pole?

13. A cell is formed in which one electrode is a saturated calomel electrode and the other consists of hydrogen gas, at 1 atm., in contact with a solution of unknown pH. The potential of the cell, at 25°C., is 0.492 volt, the calomel electrode being the positive pole. What is the pH of the unknown solution?

14. The potential, at 25°C., of the following cell

$$Pt + H_2 \ (1 \text{ atm.}) \mid H_3O^+ \ (?m) \parallel KCl \ (0.1N) \mid Hg_2Cl_2 + Hg$$
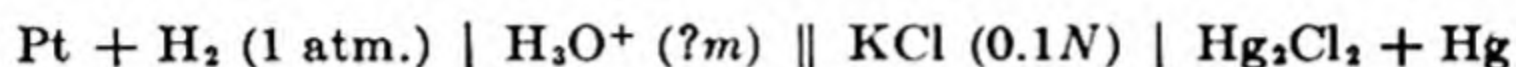
is $+0.650$ volt. What is the pH of the solution at the left-hand electrode?

15. Calculate the potential, at 25°C., of the following cell:

$$Hg + Hg_2Cl_2 \mid KCl \ (\text{satd.}) \parallel H_3O^+ \ (0.027m) + QH \mid Pt$$

16. A cell is formed in which one electrode is a decinormal calomel electrode and the other is a quinhydrone electrode in a solution of unknown pH. At 25°C. the potential of the cell is 0.020 volt, the quinhydrone electrode being the positive pole. What is the pH of the unknown solution?

17. A glass electrode was prepared by putting inside a glass membrane a solution of hydrochloric acid and inserting into this a silver electrode coated with silver chloride. A cell was formed by putting this electrode into a solution whose pH $= 3.0$ and using a decinormal calomel electrode for the other pole of the cell. At 25°C. the potential of this cell was 0.163 volt, the glass electrode being the negative pole. What is the value of $E°$ for the glass electrode?

18. A glass electrode for which the value of $E° = -0.352$ volt was inserted into a solution of unknown pH, and a cell was formed using a normal calomel electrode for the other pole. The potential of this cell, at 25°C., was 0.327 volt, the calomel electrode being the positive pole. What was the pH of the unknown solution?

19. Calculate the values of pH at which the indicator bromphenol blue exists in the following fractions in the basic form: 0.001, 0.01, 0.1, 0.2, 0.5, 0.8, 0.9, 0.99, 0.999. Draw the curve for this indicator by plotting x against pH.

20. Calculate the pH of $0.50M$ ammonium chloride. Which of the indicators in Table 9-2 is best suited to show the end point of the reaction when $1.0M$ ammonium hydroxide is titrated with $1.0M$ hydrochloric acid?

21. Calculate the pH of $0.01M$ potassium acetate. Which of the indicators in Table 9-2 is best suited to show the end point of the reaction when $0.02M$ acetic acid is titrated with $0.02M$ potassium hydroxide?

22. The color in a solution of unknown pH containing 17 drops of bromthymol blue is matched by that seen through two tubes, one containing 11 drops of the indicator in sodium hydroxide, the other containing 6 drops of the indicator in hydrochloric acid. What is the pH of the unknown solution?

23. Calculate the pH of a buffer containing 0.020 mole of sodium acetate and 0.070 mole of acetic acid per liter.

24. How much solid sodium acetate should be added to 500 ml. of 0.10M acetic acid to give a buffer with a pH of 5.1?

25. What is the value of the ratio $[HCO_3^-]/[H_2CO_3]$ in the blood?

26. From the data in Table 7-2 calculate the pH of a buffer containing 0.030 mole of sodium dihydrogen phosphate and 0.040 mole of disodium hydrogen phosphate per liter.

27. It is desired to prepare a buffer with a pH $= 5.5$. In order to have the buffer as efficient as possible, which of the acids listed in Table 7-2 should you use with its salt in preparing the buffer? In what proportions should the acid and its salt be mixed?

28. A buffer contains 0.200 mole of carbonic acid and 0.100 mole of sodium bicarbonate per liter. What change in the pH of this buffer would be caused by the addition of 0.001 mole of hydrogen chloride to 1 liter of the buffer?

29. A buffer contains 0.10 mole of ammonia and 0.30 mole of ammonium chloride per liter. What is its pH?

30. What are the buffer capacities of the buffers described in Probs. 23, 24, 26, and 29?

31. What is the average buffer capacity of the buffer in Table 9-4 between the limits pH $= 4.83$ and pH $= 5.49$?

32. What will be the buffer capacity of the buffer in Prob. 23 following the addition of 0.01 mole of sodium hydroxide to 1 liter of the buffer?

33. What will be the buffer capacity of the buffer described in Prob. 28 following the addition of 0.040 mole of hydrogen chloride to 1 liter of the buffer?

CHAPTER 10

OXIDATION AND REDUCTION

Oxidation may be defined as a loss of electrons, reduction as a gain of electrons. The application of these definitions to reactions involving ions is easy to visualize. Consider the reaction

$$Ce^{++++} + Fe^{++} \rightleftharpoons Ce^{+++} + Fe^{+++}$$
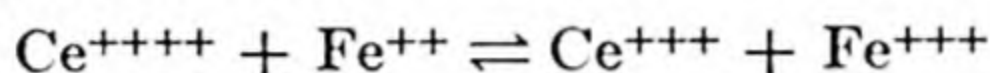
Each ferrous ion loses one electron; therefore, the ferrous ion is oxidized. The electron so released is picked up by the ceric ion, which is thereby reduced. The ferrous ion is known as the *reductant*, the ceric ion as the *oxidant*. This reaction is an example of that class of oxidation-reduction reactions that does not involve the production or consumption of hydronium ions. The free energy change and direction of such reactions are not influenced by the pH of the solution in which they take place, unless changes in pH result in the formation of slightly soluble substances, or slightly ionized complexes. For example, in the reaction cited, ferric hydroxide is less soluble than ferrous hydroxide; therefore, an increase in the pH of the solution to the point where a precipitate is formed will affect the change of free energy in the reaction and will displace the equilibrium point in the direction of the ferric ion.

Consider now the reaction

$$HAsO_2 + I_3^- + 4H_2O \rightleftharpoons H_3AsO_4 + 3I^- + 2H_3O^+$$
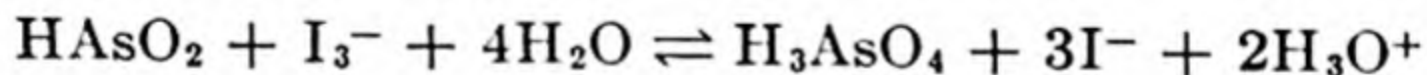
Arsenious acid is the reductant; tri-iodide ion is the oxidant. This reaction results in the production of hydronium ions. The free energy change and the direction of the reaction depend upon the pH of the solution in which it is carried on. A high pH drives it forward; a low pH drives it backward.

THE ENERGY OF OXIDATION-REDUCTION REACTIONS

The energy produced by oxidation-reduction reactions may be measured and expressed in a variety of ways, of which we shall consider two, *calorimetry* and *potentiometry*.

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Calorimetry. The heat energy released by a reaction, such as the oxidation of carbon, may be measured by allowing the reaction to take place in a calorimeter. This is a well-insulated vessel, so designed that the heat released by the reaction is entirely absorbed by a known mass of water. If the rise in temperature of the water is measured, then the heat energy released by the reaction is equal to the heat capacity of the water multiplied by the temperature rise.

The heat energy released in any such reaction will be affected by the number of moles of substance reacting, by the temperature at which the reaction takes place, and also by whether or not any change in pressure or volume occurs during the reaction. For complete clarity, therefore, all these pertinent conditions must be stated.

If the reaction occurs in a constant-volume calorimeter the heat evolved is a measure of the *decrease in internal energy* in the reaction. For example, the statement

$$2C \text{ (s)} + O_2 \text{ (g)} \rightarrow 2CO \text{ (g)} \qquad \Delta E_{25°C.} = q_v = -53,424 \text{ cal.}$$

means that if 2 gram-atoms (24 g.) of solid carbon, at 25°C., unite with 1 mole (32 g.) of gaseous oxygen to produce 56 g. of gaseous carbon monoxide, at 25°C., and if the reaction occurs at constant volume, the heat evolved is 53,424 cal.

If, on the other hand, the reaction occurs at constant pressure, the heat evolved is a measure of the *decrease in enthalpy* in the reaction. This may be quite different from the heat evolved at constant volume, because of the energy involved in any volume changes that may occur. For example,

$$2C \text{ (s)} + O_2 \text{ (g)} \rightarrow 2CO \text{ (g)} \qquad \Delta H_{25°C.} = q_p = -52,832 \text{ cal.}$$

The amount of energy released in an oxidation, as in any other reaction, is independent of the path followed in going from the initial to the final state. Thus, if sugar is oxidized to carbon dioxide and water, the number of calories released per mole of sugar is the same whether the oxidation takes place in a calorimeter or in the human body, provided that the initial substances, the products, the temperature, and the pressure are the same in both cases.

Potentiometry. If an oxidation-reduction reaction can be so arranged that electrons are released at one end of a conductor and absorbed at the other, it should then be possible to measure the

electrical energy evolved by the reaction. As we have seen in Chap. 8, if this measurement is carried out so that the reaction occurs reversibly, the observed potential is a measure of the *decrease in free energy* in the reaction. Since this decrease in free energy is affected by the temperature of the reaction and by the concentrations of the reactants, it is necessary to specify these. Thus, the expression

$$Ce^{++++} (0.1m) + Fe^{++} (0.01m) \rightleftharpoons Ce^{+++} (1.0m) + Fe^{+++} (0.01m)$$
$$E_{25°c.} = +0.78 \text{ volt}$$
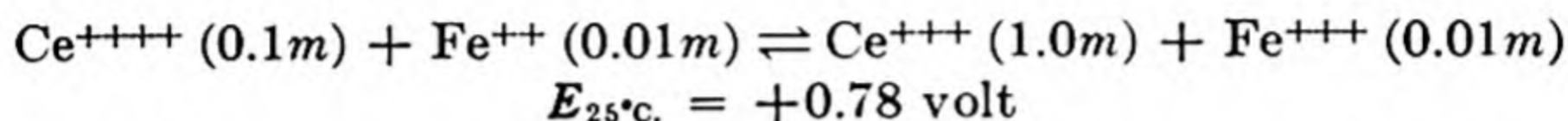
means that if a cell is formed, containing at one electrode a solution that is 0.1 molal with respect to ceric ion and 1.0 molal with respect to cerous ion, and at the other electrode a solution which is 0.01 molal with respect to both ferrous and ferric ions, the potential of the cell, at 25°C., is 0.78 volt. The convention concerning the sign of the potential for an oxidation-reduction reaction like that shown above is that a positive potential indicates that the reaction, as written, will go forward spontaneously with a decrease in free energy; a negative potential means that the reaction will go backward spontaneously, but will not go forward unless driven by the imposition of an external potential.

The decrease in free energy accompanying the reaction shown above can be computed by using the expression

$$\Delta F = -nFE$$

Since the reaction involves the transfer of a single electron from a ferrous ion to a ceric ion, $n = 1$. Hence,

$$\Delta F = -1 \times 96{,}500 \times 0.78 = -75{,}000 \text{ joules}$$
$$= -18{,}000 \text{ cal.}$$

Since the spontaneous reaction involves the transfer of electrons from ferrous ions to ceric ions it follows that the electrode containing the ferrous and ferric solutions will be the negative pole of the cell.

OXIDATION-REDUCTION POTENTIALS

Redox Couples. Let us refer again to the oxidation-reduction reaction:[1]

$$Ce^{++++} + Fe^{++} \rightleftharpoons Fe^{+++} + Ce^{+++}$$

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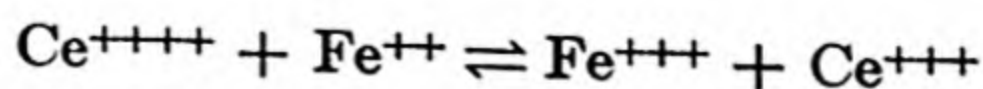
[1] For economy of space, the name *redox* has been coined to replace oxidation-reduction. We shall so use it in the future.

In this reaction, an electron leaves the ferrous ion, thus converting it into ferric ion. This change represents half the total change in the above equation. It is, therefore, known as a *half-reaction* and is usually written

$$Fe^{++} \rightleftharpoons Fe^{+++} + e$$
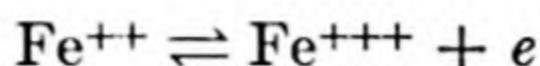
Ferrous ion is a reductant. Ferric ion is an oxidant and is derived from ferrous ion by the removal of an electron. When an oxidant and reductant are so related, they are said to be *conjugate* to each other. Such a combination of conjugate oxidant and reductant is known as a *redox couple*.

The electrons released by this couple cannot remain unattached, but must be absorbed by some other couple that is capable of accepting them. In the above case, this is the ceric-cerous ion couple for which the half-reaction is

$$Ce^{+++} \rightleftharpoons Ce^{++++} + e$$

Thus any oxidation-reduction reaction occurs between two redox couples, one of which is an electron donor or reductant, the other of which is an electron acceptor or oxidant. There can be no oxidation without an equivalent reduction. The complete reaction is the sum of the two half-reactions for the couples concerned.

In writing half-reactions we shall follow the convention that the oxidant shall appear on the right-hand side of the reaction as written. Thus the general expression for a half-reaction is

$$\text{Red} \rightleftharpoons \text{Ox} + ne \tag{10-1}$$

where n is the number of electrons released in the reaction. An example of a more complex half-reaction is that for the manganous-permanganate ion couple.

$$Mn^{++} + 12H_2O \rightleftharpoons MnO_4^- + 8H_3O^+ + 5e$$

The general form for a complete redox reaction is

$$a\text{Ox}_1 + b\text{Red}_2 \rightleftharpoons a\text{Red}_1 + b\text{Ox}_2 \tag{10-2}$$
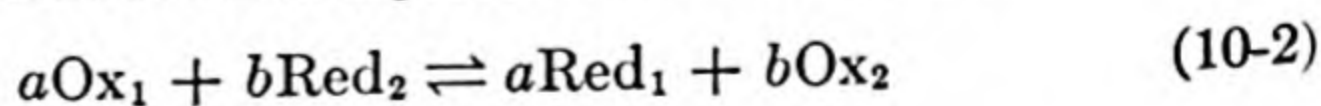
In Eq. (10-2) the substances with the same subscript are conjugate to each other. The numbers represented by a and b are such that the number of electrons released by the reductant

couple is equal to that absorbed by the oxidant couple. For example,

$$MnO_4^- + 8H_3O^+ + 5Fe^{++} \rightleftharpoons Mn^{++} + 12H_2O + 5Fe^{+++}$$

$$\begin{array}{cccc} 1Ox_1 & 5Red_2 & 1Red_1 & 5Ox_2 \\ a & b & a & b \end{array}$$
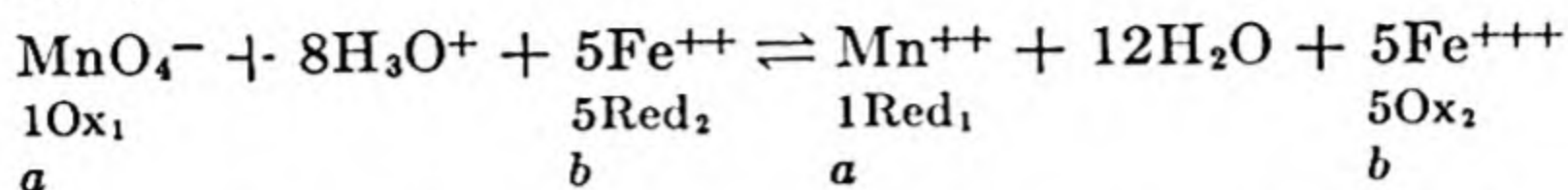
The potential of any redox reaction is determined by the difference between the potentials with which the two couples concerned release electrons. That couple which releases electrons with the more positive potential will compel the other couple to accept them. Thus the first couple becomes oxidized; the second couple becomes reduced. The potential with which each couple releases electrons is known as its *redox potential*, for which the symbol is E_R. The potential of the complete reaction is equal to the difference between the redox potentials of the two couples concerned.

Redox Potentials. The redox potentials of many couples[1] may be determined by measuring the potential with which they donate electrons to, or accept electrons from, some couple that has been chosen as a standard.

The standard redox couple is one that we have met before, *viz.*, hydrogen gas, at 1 atm., in contact with hydronium ion at unit activity. The redox potential of this couple is 0.0 volt.

Consider now the cell

$$Pt \mid Ce^{++++}(1.0m) + Ce^{+++}(1.0m) \mid KCl \mid H_3O^+(1.0m) \mid H_2(1\,atm.) + Pt$$
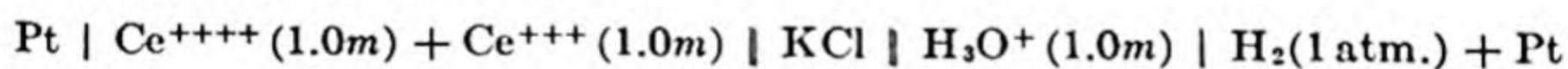
The potential of this cell may be measured on the potentiometer shown in Fig. 9-7. At 25°C. the cell shows a potential of -1.61 volts.

In accordance with the conventions stated in Chap. 9 for cell potentials, the minus sign indicates that the right-hand electrode of the cell, as written, is negative. In other words, electrons flow, through a wire joining the electrodes, from the hydrogen-hydronium ion couple to the cerous-ceric ion couple. We say that the cerous-ceric ion couple is poorer as an electron donor than is the hydrogen-hydronium ion couple by 1.61 volts, and we indicate this fact by stating that the redox potential of the

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[1] Only the potential of couples in which the reaction Red $\rightleftharpoons$ Ox $+ ne$ is electrochemically reversible may be measured in this way. The potential of the couple oxalate ion–carbon dioxide cannot be so measured because the reaction $C_2O_4^{--} \rightarrow 2CO_2 + 2e$ is not reversible in an electrochemical cell.

cerous-ceric ion couple, at 25°C., is -1.61 volts. Since this value is for the case when each ion is in its standard state, we say that this is the *standard redox potential* for the couple and indicate it by the symbol $E°$.

Consider now the cell

$$\text{Pt} + \text{H}_2 \text{ (1 atm.)} \mid \text{H}_3\text{O}^+ \text{ (1.0}m\text{)} \mid \text{KCl} \mid \text{V}^{++} \text{ (1.0}m\text{)} + \text{V}^{+++} \text{ (1.0}m\text{)} \mid \text{Pt}$$

The potential, at 25°C., of this cell is -0.20 volt; *i.e.*, the right-hand electrode is negative. This means that the vanadous-vanadic ion couple is more powerful as an electron donor than is the hydrogen-hydronium ion couple by 0.20 volt. We indicate this fact by stating that the standard redox potential of the vanadous-vanadic ion couple is $+0.20$ volt.

TABLE 10-1. STANDARD REDOX POTENTIALS OF SOME REDOX COUPLES
AT 25°C.

Half-reaction	$E°$, volts
$\text{Cr}^{++} \rightleftharpoons \text{Cr}^{+++} + e$	$+0.41$
$\text{V}^{++} \rightleftharpoons \text{V}^{+++} + e$	$+0.20$
$\text{H}_2 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_3\text{O}^+ + 2e$	±0.00
$\text{Sn}^{++} \rightleftharpoons \text{Sn}^{++++} + 2e$	-0.15
$\text{Fe(CN)}_6^{----} \rightleftharpoons \text{Fe(CN)}_6^{---} + e$	-0.36
$4\text{OH}^- \rightleftharpoons 2\text{H}_2\text{O} + \text{O}_2 + 4e$	-0.40
$\text{MBH}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{MB} + 2\text{H}_3\text{O}^+ + 2e^*$	-0.53
$3\text{I}^- \rightleftharpoons \text{I}_3^- + 2e$	-0.54
$\text{HAsO}_2 + 4\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{AsO}_4 + 2\text{H}_3\text{O}^+ + 2e$	-0.56
$\text{C}_6\text{H}_4(\text{OH})_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_4\text{O}_2 + 2\text{H}_3\text{O}^+ + 2e$	-0.699
$\text{Fe}^{++} \rightleftharpoons \text{Fe}^{+++} + e$	-0.77
$6\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 4\text{H}_3\text{O}^+ + 4e$	-1.23
$\text{Mn}^{++} + 12\text{H}_2\text{O} \rightleftharpoons \text{MnO}_4^- + 8\text{H}_3\text{O}^+ + 5e$	-1.52
$\text{Ce}^{+++} \rightleftharpoons \text{Ce}^{++++} + e$	-1.61

* The formulas MBH_2 and MB represent respectively the reduced and oxidized forms of methylene blue.

These standard redox potentials are for the case when each substance involved in the half-reaction is in its standard state. Any couple will reduce a couple whose redox potential is more negative but will oxidize any couple whose redox potential is more positive.

For the calculation of the values of the redox potential when the substances are not in their standard states, we use an equation that is similar to Eq. (9-7). For the half-reaction expressed in Eq. (10-1), the redox potential is given by the expression

$$E_R = E° - 2.303 \frac{RT}{nF} \log \frac{[\text{Ox}]}{[\text{Red}]} \tag{10-3}$$

from which, for the potential at 25°C., we get the expression

$$E_R = E° - \frac{0.059}{n} \log \frac{[Ox]}{[Red]} \qquad (10\text{-}4)$$

in which n represents the number of electrons released in the half-reaction for the couple as written.

Example. What is the value of the redox potential for the following electrode?

$$Pt \mid Sn^{++} \ (0.05m) + Sn^{++++} \ (0.1m)$$
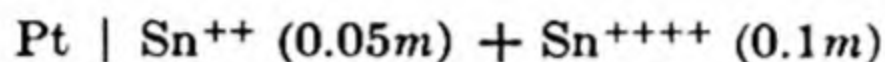
The half-reaction for the couple is

$$Sn^{++} \ (0.05m) \rightleftharpoons Sn^{++++} \ (0.1m) + 2e$$
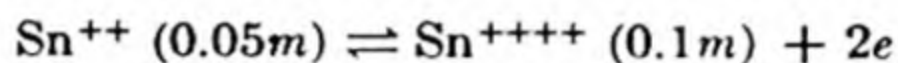
The redox potential is given by the expression

$$E_R = E° - \frac{0.059}{2} \log \frac{[Sn^{++++}]}{[Sn^{++}]}$$

$$E_R = -0.15 - 0.0295 \log \frac{0.1}{0.05}$$

$$E_R = -0.15 - 0.0295 \times 0.30$$

$$E_R = -0.15 - 0.0089 = -0.16 \text{ volt}$$

It is sometimes desirable to portray the conduct of redox couples by graphs in which the redox potential is plotted against the per cent of the couple in the oxidized form. The simplest such case is that in which the oxidized and reduced form of the couple each consists of a single ion. In drawing or interpreting graphs for these simple cases, it will be helpful to note the following facts:

1. When the couple is 50 per cent in the oxidized form, the concentrations of the oxidized and reduced forms are equal to each other, and, therefore, the value of the redox potential is equal to $E°$.

2. For each tenfold change in the value of the ratio $[Ox]/[Red]$, the value of the redox potential changes by $0.059/n$ volt. Therefore, the curves for those couples for which n equals 1 will have slopes that are greater than those for couples for which n equals 2. This is illustrated in Fig. 10-1.

A knowledge of the values of the redox potentials for various couples enables us to calculate the direction and free energy change of redox reactions.

Example. What is the direction and change in free energy in the following redox reaction?

$$Sn^{++} \ (0.20m) + 2V^{+++} \ (0.10m) \rightleftharpoons Sn^{++++} \ (0.30m) + 2V^{++} \ (0.050m)$$
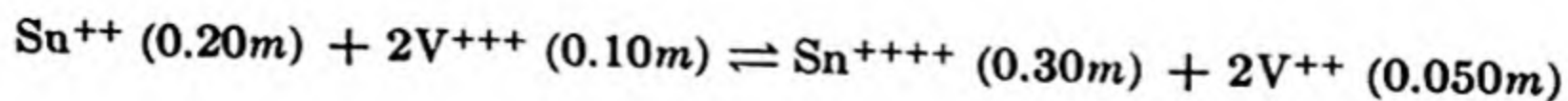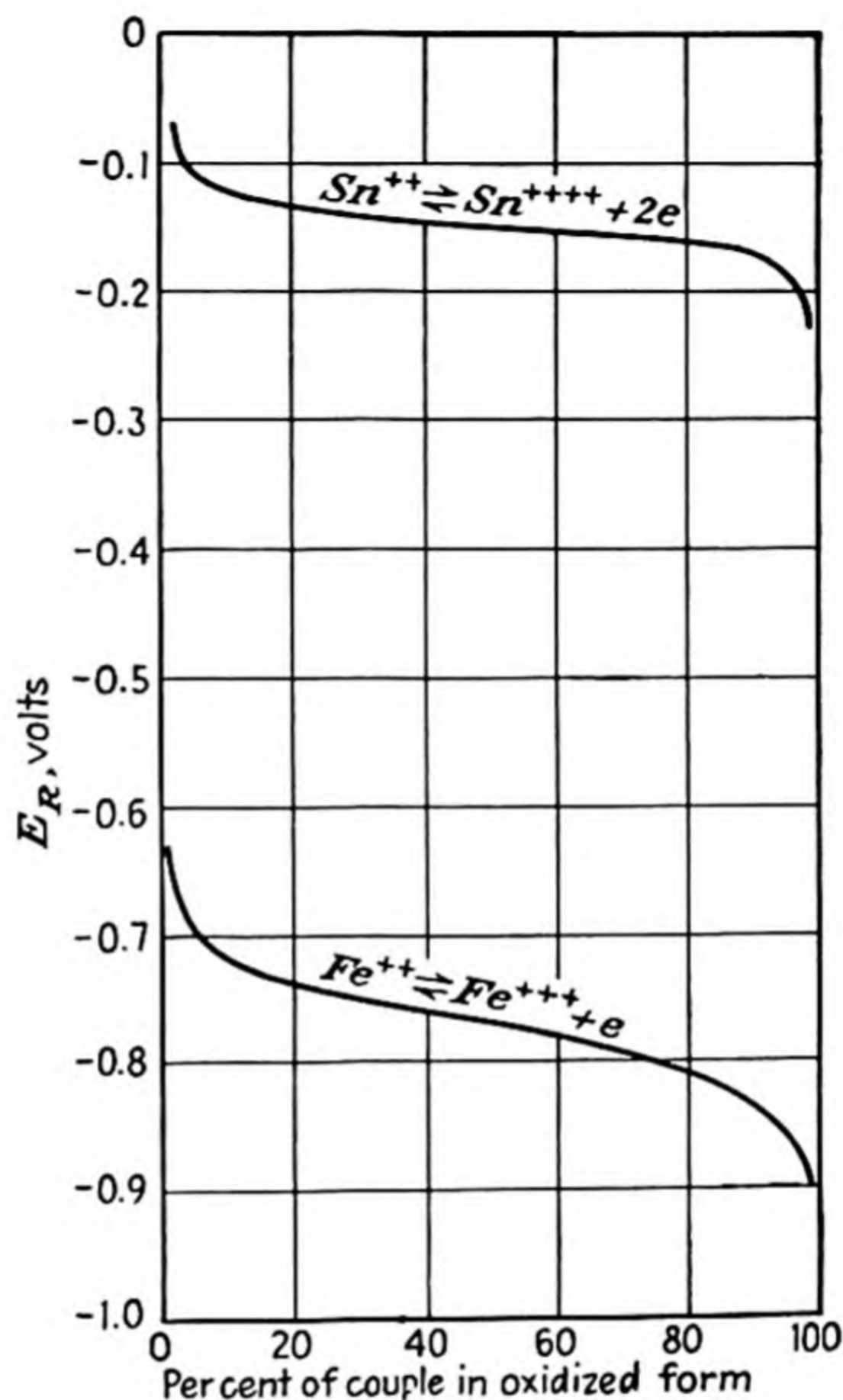
FIG. 10-1.   Redox potential curves.

Imagine a cell composed of these two couples, as follows:

Pt | Sn^{++} (0.20m) + Sn^{++++} (0.30m) | KCl | V^{++} (0.050m)

$+ V^{+++}$ (0.10m) | Pt
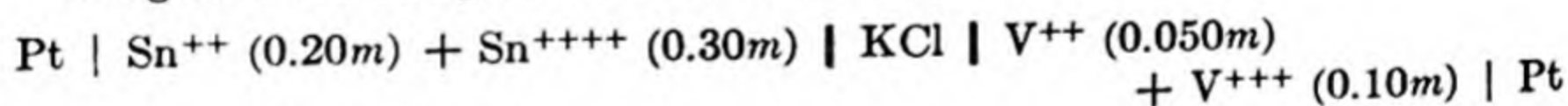
The potential of this cell is

$$E_{cell} = E_{left} - E_{right}$$

$$E_{cell} = \left(E_{Sn}^{\circ} - \frac{0.059}{2} \log \frac{[Sn^{++++}]}{[Sn^{++}]} \right) - \left(E_{V}^{\circ} - 0.059 \log \frac{[V^{+++}]}{[V^{++}]} \right)$$

$$E_{cell} = (-0.15 - 0.0295 \log 1.5) - (+0.20 - 0.059 \log 2.0)$$

$$E_{cell} = -0.34 \text{ volt}$$

The negative sign of the cell potential means that the vanadous-vanadic ion couple forms the negative pole of the cell.   Electrons flow spontaneously from the right-hand electrode to the left-hand electrode with a potential of 0.34 volt.   In other words, the spontaneous reaction is the reduction of stannic ion and the oxidation of vanadous ion.   We would say, therefore,

that the potential of the original redox reaction, as written, is −0.34 volt. In this case, the negative value indicates that the reaction, as written, will not go forward spontaneously, but will require the imposition of an outside potential. The increase in free energy as the reaction goes forward is

$$\Delta F = -nFE = -2 \times 96,500 \times -0.34 = +66,000 \text{ joules} = +16,000 \text{ cal.}$$

Equilibrium in Redox Reactions. In any redox reaction, if the standard redox potential of the oxidant couple is subtracted from the standard redox potential of the reductant couple, the result is the standard redox potential for the complete reaction, *i.e.*, the potential developed when each substance involved in the reaction is in its standard state.

The standard redox potential for the reaction can be used in an equation similar to Eq. (9-10) to calculate the standard free energy change in the reaction.

$$\Delta F^\circ = - nFE^\circ \tag{10-5}$$

By combining Eq. (10-5) with Eq. (8-21) we can obtain a relation between the standard redox potential for a reaction and its equilibrium constant.

$$\log K = \frac{nFE^\circ}{2.303RT} \tag{10-6}$$

At 25°C. Eq. (10-6) may be simplified to

$$\log K = \frac{nE^\circ}{0.059} \tag{10-7}$$

Example. State the standard free energy change and the value of the equilibrium constant, at 25°C., for the reaction

$$5Fe^{++} + MnO_4^- + 8H_3O^+ \rightleftharpoons 5Fe^{+++} + Mn^{++} + 12H_2O$$
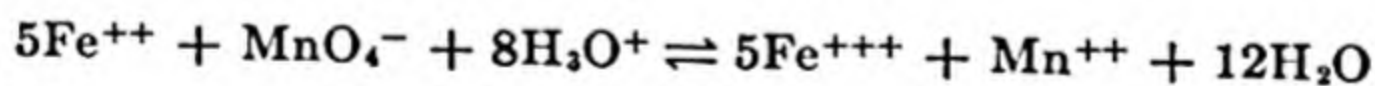
Ferrous ion is the reductant; permanganate ion is the oxidant.

$$E^\circ_{reaction} = E^\circ_{Fe} - E^\circ_{Mn} = (-0.77) - (-1.52) = +0.75 \text{ volt}$$
$$\Delta F^\circ = -nFE^\circ = -5 \times 96,500 \times 0.75 = -360,000 \text{ joules}$$
$$\Delta F^\circ = -86,000 \text{ cal.}$$
$$\log K = \frac{nE^\circ}{0.059} = \frac{5 \times 0.75}{0.059} = 63$$
$$K = 10^{63}$$

Redox Indicators. The redox potential of a couple can be determined by measuring the potential of a cell in which the couple forms one electrode and the other electrode is a couple

whose redox potential is known. Redox potentials may also be determined by the use of *redox indicators*. These indicators are reversible redox couples in which the color of the oxidant differs from that of the reductant. While these couples may be composed of inorganic substances, such as the manganous-permanganate ion couple, they are usually complex organic systems, of which methylene blue is a typical example.

To be useful, the indicator should be one in which equilibrium between the oxidized and reduced forms is attained rapidly. If a small amount of such an indicator is placed in a solution whose redox potential is to be measured, the indicator will either accept electrons from, or donate electrons to, the solution until the redox potential of the indicator equals that of the solution. If the original quantity of oxidant and reductant in the solution was large compared with the amount of indicator added, this transfer of electrons will cause no appreciable change in the redox potential of the solution.

Methylene blue is the oxidant of a couple whose reductant, methylene white, is colorless in solution.

Methylene white
reductant

Methylene blue
oxidant
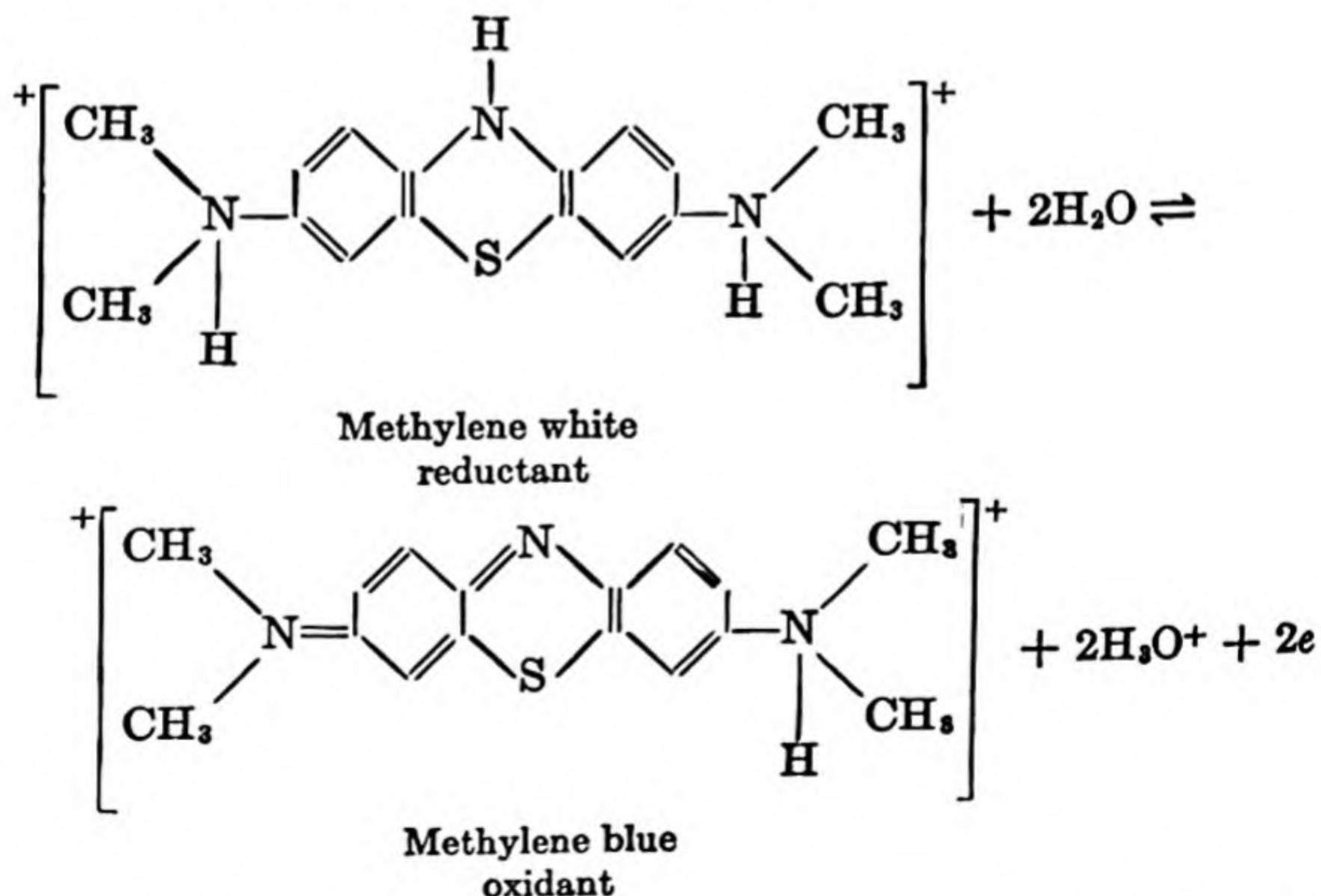
This half-reaction is usually written in some abbreviated form, such as

$$MBH_2 + 2H_2O \rightleftharpoons MB + 2H_3O^+ + 2e$$
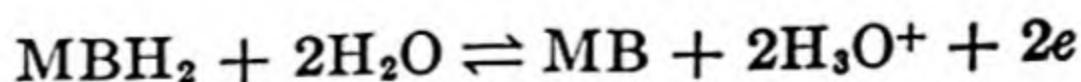
The expression for the redox potential of this couple is

$$E_R = E° - \frac{0.059}{2} \log \frac{[MB][H_3O^+]^2}{[MBH_2]}$$

This expression may be rewritten to read

$$E_R = E° - \frac{0.059}{2} \log \frac{[MB]}{[MBH_2]} - 0.059 \log [H_3O^+] \quad (10\text{-}8)$$

From Eq. (10-8) it appears that the redox potential of methylene blue depends upon two factors: (1) the value of the ratio $[MB]/[MBH_2]$, and (2) the pH of the solution. If we hold constant the value of the ratio $[MB]/[MBH_2]$, then the value of the redox potential is a function of the pH of the solution. If we hold the pH of the solution constant by use of a buffer, the value of the redox potential is a function of the value of the ratio $[MB]/[MBH_2]$.

Since we shall be particularly interested in the relationship between the redox potential and the value of the ratio $[MB]/[MBH_2]$, we can rewrite Eq. (10-8) to read

$$E_R = E°' - \frac{0.059}{2} \log \frac{[MB]}{[MBH_2]} \quad (10\text{-}9)$$

In Eq. (10-9), $E°'$ is equal to $E° - 0.059 \log [H_3O^+]$. Unfortunately, the value of $E°$ does not remain constant as the pH of the solution changes; hence the value of $E°'$ does not change regularly with changes in pH. Consequently, the value of $E°'$ must be determined experimentally at various values of pH. Table 10-2 shows the values of $E°'$ for methylene blue[1] at different values of pH. These values are plotted in Fig. 10-2.

TABLE 10-2. APPROXIMATE VALUES OF $E°'$ FOR METHYLENE BLUE AT SEVERAL VALUES OF pH

pH	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
$E°'$	−0.53	−0.44	−0.36	−0.27	−0.19	−0.10	−0.05	−0.01	+0.02	+0.05

[1] For the values of $E°'$ for other redox indicators, the reader is referred to W. M. Clark, "The Determination of Hydrogen Ions," 3d ed., p. 683, The Williams & Wilkins Company, Baltimore, 1928.

If now a solution of methylene blue is buffered at a certain value of pH we can, by the use of Eq. (10-9), calculate the redox potential of the solution corresponding to various values of the ratio [MB]/[MBH$_2$] at that pH. The values so obtained when pH = 0.0 are plotted in the bottom curve in Fig. 10-3. Repetition of this process at a different value of pH results in a curve having the same shape but displaced up or down the potential axis. Figure 10-3 shows a series of such curves.
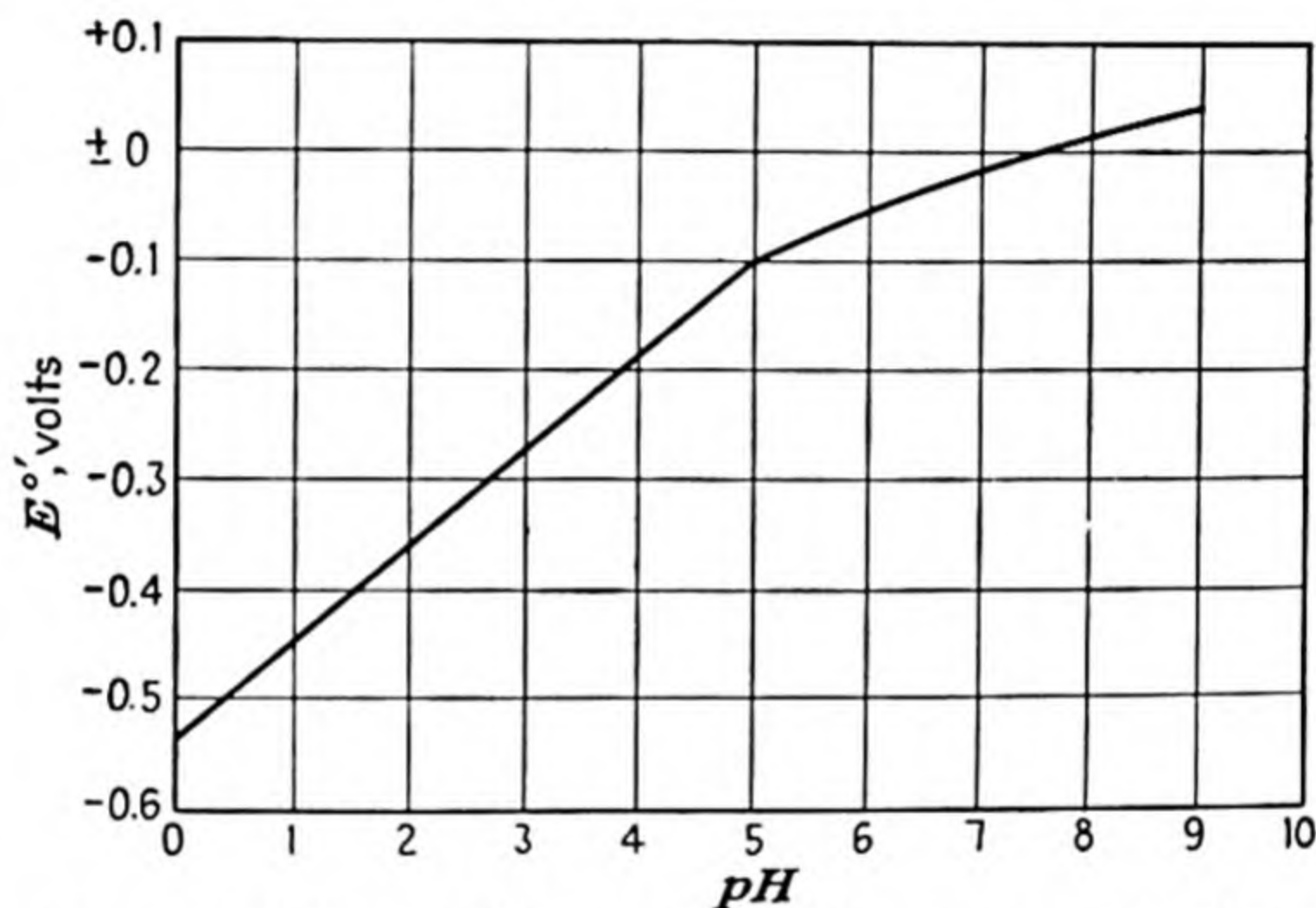
Fig. 10-2. Values of $E^{o\prime}$ for methylene blue at several pH values.

Since the reduced form of methylene blue is colorless, while the oxidized form is blue, variations of the percentage of the substance in the oxidized form should correspond to varying shades of blue. It should thus be possible to prepare a series of standards containing differing proportions of the oxidized and reduced forms of the indicator, but having the same total concentration of indicator in each, and these solutions should show different shades of color.

The redox potential of an unknown solution may be determined by adding to it the same total concentration of methylene blue as was used in preparing the standards. The color of this solution can then be matched against that of the standards and the percentage of the indicator in the oxidized form determined. This may be used to find the value of the ratio [MB]/[MBH$_2$] in the solution. A determination of the pH of the solution will

show which value of $E^{\circ'}$ to use. The substitution of these data in Eq. (10-9) will give the redox potential of the solution.

Best results will be obtained from this method if an indicator is chosen whose $E^{\circ'}$ value is near to the redox potential of the unknown solution. This means that in the solution there will be approximately equal amounts of the indicator in the oxidized and reduced forms. It is in this region that the indicator is most sensitive. For example, examination of Fig. 10-3 shows
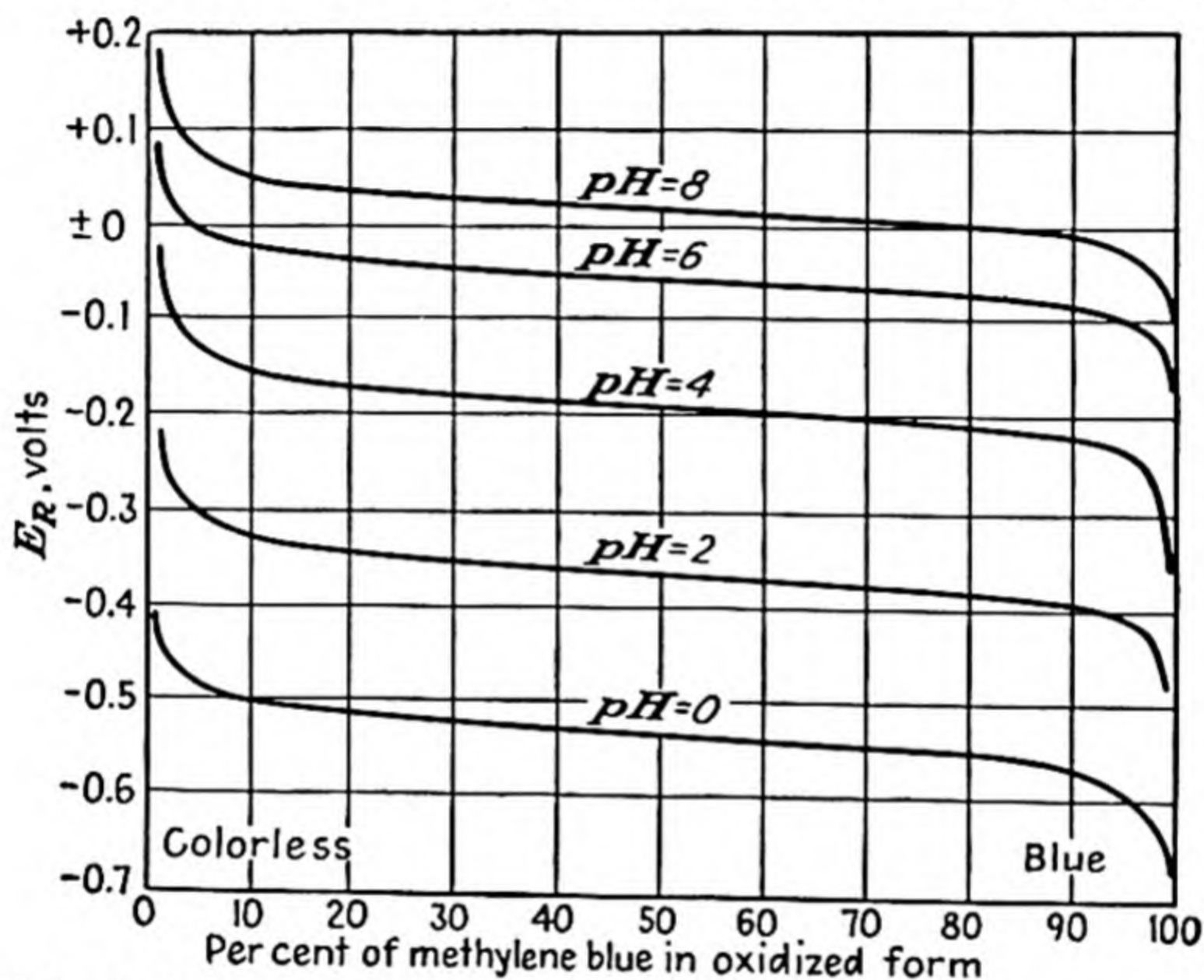
Fig. 10-3. Redox potential curves for the indicator methylene blue at several pH values.

that, at a pH equal to 2.0, methylene blue would be useless as an indicator in solutions whose redox potential lay outside the range -0.3 to -0.4 volt.

Example. It is desired to find the redox potential of a solution whose pH = 4.0. A small amount of methylene blue is added to the solution. Comparison with a series of standards shows that 40 per cent of the indicator is in the oxidized form. From this we find that the value of the ratio [MB]/[MBH$_2$] is 0.67. When the pH is 4.0, the value of $E^{\circ'}$ to be used is -0.19. Substitution of these data in Eq. (10-9) gives

$$E_R = -0.19 - \frac{0.059}{2} \log 0.67$$

$$E_R = -0.19 - (0.0295 \times -0.17)$$

$$E_R = -0.19 + 0.005 = -0.185 \text{ volt}$$

The change of color of methylene blue with change in redox potential may be demonstrated by the following experiment. A few drops of methylene blue solution are added to a flask containing a solution of glucose that has been made alkaline with sodium hydroxide. The redox potential of the alkaline glucose is sufficiently high to reduce and decolorize the methylene blue. If the flask is now shaken so that some air dissolves in the solution, the oxygen of the air will oxidize the methylene white, causing the solution to turn blue. Upon standing, the glucose will once more reduce and decolorize the indicator. This process may be repeated until the concentration of the glucose has been decreased to the point where it will no longer reduce methylene blue.

Problems

1. Interpret the following expression:

$$C_6H_{12}O_6 \text{ (s)} + 6O_2 \text{ (g)} \rightarrow 6CO_2 \text{ (g)} + 6H_2O \text{ (l)}, \quad q_p \text{ (20°C.)} = -673,000 \text{ cal.}$$

2. Interpret the following expression:

$$Cr^{+++} \text{ (0.01}m\text{)} + Cu^+ \text{ (0.1}m\text{)} \rightleftharpoons Cr^{++} \text{ (0.02}m\text{)} + Cu^{++} \text{ (0.03}m\text{)}$$
$$E_{25°C.} = -0.56 \text{ volt}$$
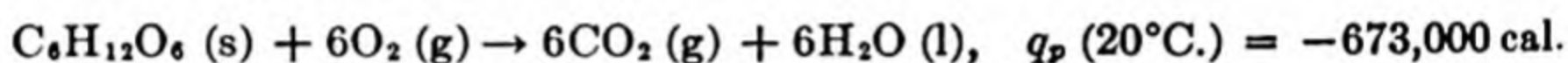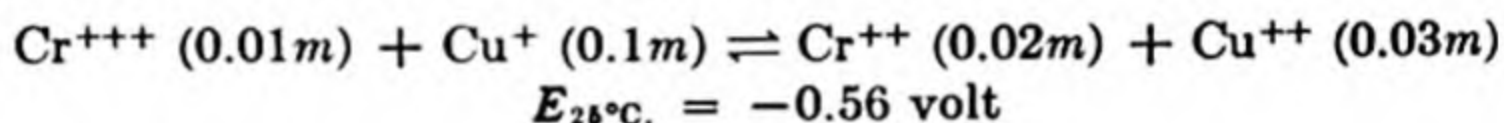
3. Calculate the free energy change in the reaction in Prob. 2.

4. Calculate the redox potential, at 25°C., of the couple whose half-reaction is

$$Fe^{++} \text{ (0.030}m\text{)} \rightleftharpoons Fe^{+++} \text{ (0.15}m\text{)} + e$$
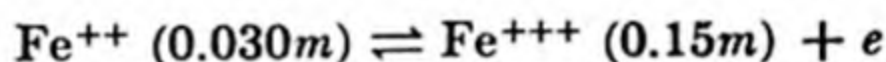
5. Calculate the redox potential, at 25°C., for the couple whose half-reaction is

$$HAsO_2 \text{ (0.10}m\text{)} + 4H_2O \rightleftharpoons H_3AsO_4 \text{ (0.040}m\text{)} + 2H_3O^+ \text{ (0.050}m\text{)} + 2e$$
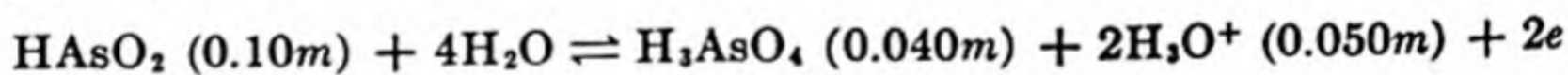
6. Calculate the redox potential, at 25°C., for the electrode

$$Pt \mid Sn^{++} \text{ (0.20}m\text{)} + Sn^{++++} \text{ (0.050}m\text{)}$$
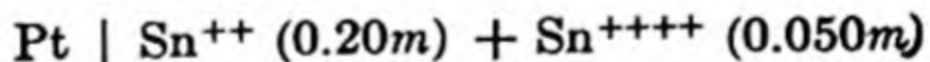
7. It is desired to measure the potential of the reaction

$$2Fe^{++} \text{ (0.20}m\text{)} + Sn^{++++} \text{ (0.050}m\text{)} \rightleftharpoons 2Fe^{+++} \text{ (0.010}m\text{)} + Sn^{++} \text{ (0.10}m\text{)}$$
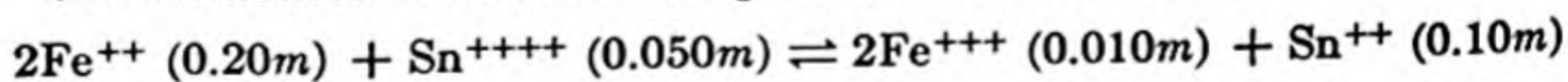
Draw the diagram of a cell in which this reaction takes place. Calculate the potential, at 25°C., of the cell, and tell in which direction the above reaction goes spontaneously.

8. Calculate the change in free energy in the reaction in Prob. 7.

9. In the following reaction show that if the pH is 0.0 the reaction will go to the left spontaneously; if the pH is 1.0 the reaction will go to the right spontaneously.

$$HAsO_2 \text{ (0.1}m\text{)} + I_3^- \text{ (0.001}m\text{)} + 4H_2O \rightleftharpoons H_3AsO_4 \text{ (0.1}m\text{)}$$
$$+ 3I^- \text{ (0.1}m\text{)} + 2H_3O^+$$
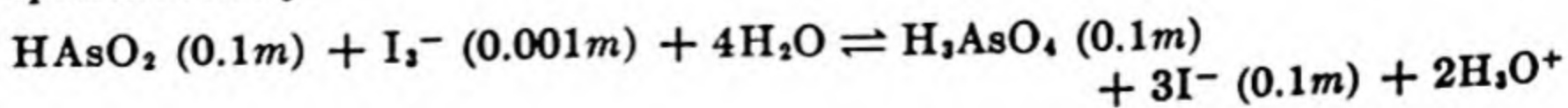
10. What is the standard free energy change and the value of the equilibrium constant, at 25°C., for the oxidation of stannous ion by ceric ion?

11. The potential, at 25°C., of the following cell is 1.52 volts, the calomel electrode being the negative pole. Calculate the value of the standard redox potential for the cobaltous-cobaltic ion couple.

$$Hg + Hg_2Cl_2 \mid KCl \ (0.1N) \mid Co^{++} \ (0.01m) + Co^{+++} \ (0.02m) \mid Pt$$
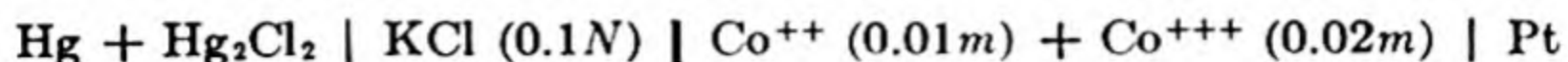
12. A solution is buffered at a pH of 7.0. A small amount of methylene blue is added. Comparison with a set of standards containing the same total concentration of methylene blue shows that the indicator is 70 per cent in the oxidized form. What is the redox potential of the solution?

13. Show that oxygen, at 0.20 atm. pressure, will oxidize the reduced form of methylene blue in a solution in which the concentrations of the reduced and oxidized forms are equal to each other and the pH is 9.0.

CHAPTER 11

SPEED OF REACTION. CATALYSIS. ADSORPTION

SPEED OF REACTION

In developing the expression for the equilibrium constant of a reversible reaction in Chap. 7, the statement was made that, at equilibrium, the forward speed is equal to the reverse speed. The speed of a reaction was stated to be equal to a constant k multiplied by the product of the concentrations of the reacting substances. No attempt was made at that time to evaluate the speed of the reaction or the constant k. These values were not essential to the determination of the value of the equilibrium constant. It is, however, frequently desirable to be able to measure reaction velocities and to determine the values of the constant k. This chapter will be concerned with the means of doing this for some simple reactions. We shall also consider some of the factors, other than concentration, that affect the speed of a reaction.

The speed of a chemical reaction may be defined as *the number of moles of substance transformed per unit volume in unit time*. The unit of volume is usually the liter. The unit of time may be of any convenient size (second, minute, hour, day, year), but the size must be definitely stated. Most reactions between ions proceed so rapidly that the measurement of their speed is difficult or impossible. For example, the reaction between hydronium ion and hydroxide ion, or between silver ion and chloride ion, is practically instantaneous. However, a few inorganic reactions and many organic reactions do proceed slowly enough so that there is some chance of measuring their velocity. To be readily susceptible of such measurement, a reaction must not only be reasonably slow, but it must also proceed practically to completion; *i.e.*, it must be irreversible.[1] The following are a few

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[1] Even for reversible reactions, it is possible to evaluate the speeds and the constants k_1 and k_2 for the forward and reverse reactions. The calculations are, however, beyond the scope of this text. For further information, see

typical reactions that satisfy these conditions, or come so close to doing so that they may be used for measurements of reaction velocities:

(1) $Ra \rightarrow Rn + He$

(2) $2N_2O_5 \rightarrow 2N_2O_4 + O_2$

(3) $2HI \rightarrow H_2 + I_2$

(4) $C_2H_5CH_3CO_2 + OH^- \rightarrow C_2H_5OH + CH_3CO_2^-$

(5) $2NO + O_2 \rightarrow 2NO_2$

(6) $C_2H_5CH_3CO_2 + H_2O \rightarrow C_2H_5OH + HCH_3CO_2$

The Molecularity of a Reaction. The *molecularity* of a reaction is determined by the number of molecules, atoms, or ions (whether of the same or different species), that must make contact simultaneously for the reaction to occur. The molecularity can sometimes be told from examination of the ordinary, balanced chemical equation for the reaction, known as the *stoichiometric equation*. This, however, is seldom the case, for the stoichiometric equation shows only the quantitative relation between the initial and final substances in the reaction. This over-all reaction may be composed of several intermediate consecutive reactions, each with its own molecularity.

The decomposition of radium can proceed without contact between atoms. This is a *unimolecular reaction*, as would appear from the stoichiometric equation (reaction 1) shown above.

The decomposition of hydrogen iodide (reaction 3) requires the simultaneous contact of two molecules of the substance. This is a *bimolecular reaction*, as would appear from its stoichiometric equation. On the other hand, the equation for the decomposition of nitrogen pentoxide (reaction 2) would indicate that it is a bimolecular reaction, but analysis of the mechanism of the reaction shows that it occurs in at least two steps,

$$N_2O_5 \rightarrow N_2O_4 + O \qquad \text{unimolecular}$$
$$O + O \rightarrow O_2 \qquad \text{bimolecular}$$
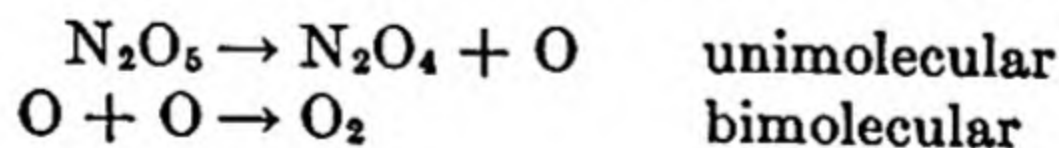
In this, as in many other cases, the reaction is more complex than is indicated by the stoichiometric equation.

The oxidation of nitric oxide (reaction 5) requires the simultaneous contact of three molecules. This is one of the few known

F. H. MacDougall, "Physical Chemistry," pp. 419–423, The Macmillan Company, New York, 1936.

examples of *termolecular* reactions.   Reactions of higher molecularity are unknown.

The Order of a Reaction.   The *order* of a reaction is the number of concentration terms to whose product the speed of the reaction is proportional.   This is not necessarily the same as the molecularity of the reaction.

The expression for the speed of the decomposition of radium may be written $k[Ra]$, indicating that it is a *first-order* reaction, as well as a unimolecular one.

The expression for the speed of decomposition of hydrogen iodide is $k[HI]^2$, indicating that it is a *second-order* reaction.   The saponification of ethyl acetate (reaction 4) is likewise second-order, since the expression for its speed is $k[C_2H_5CH_3CO_2][OH^-]$.

The expression for the speed of oxidation of nitric oxide is $k[NO]^2[O_2]$, indicating that it is a *third-order* reaction.

In the examples cited above, the orders of the reactions are the same as their molecularity.   This is not always so.   Consider the decomposition of nitrogen pentoxide.   The expression for the speed of this reaction is found to be $k[N_2O_5]$, indicating that it is a first-order reaction.   The explanation advanced for this is that when a reaction is composed of two or more steps, the order of the reaction is determined by the order of the slowest step. In this case the slowest step is the first-order reaction

$$N_2O_5 \rightarrow N_2O_4 + O$$
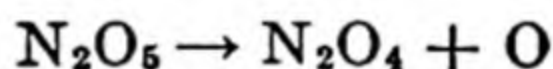
Consider the hydrolysis of ethyl acetate (reaction 6).   This is a bimolecular reaction, but if a small amount of ester is added to a large amount of water, the concentration of water remains essentially constant during the hydrolysis, the speed of the reaction is controlled by the concentration of the ester, and the expression for the speed is $k[C_2H_5CH_3CO_2]$, indicating that it is a first-order reaction.

Methods for the determination of reaction orders will be discussed in the succeeding sections.

First-order Reactions.   The law of mass action, as it applies to a first-order reaction, may be stated algebraically as follows:

$$\frac{x}{t_2 - t_1} = ka \qquad (11\text{-}1)$$

In this equation, x represents the number of moles per liter of the substance transformed during the brief time interval $t_2 - t_1$, a represents the molar concentration of the reacting substance,[1] and k represents the velocity constant. The velocity constant for a first-order reaction is defined as the fraction of the substance that is transformed in unit time. It has the dimensions of 1/time. As the reaction proceeds, the concentration of the reacting substance and, therefore, the speed of the reaction diminish, but the value of k remains constant if the temperature does not change.

It would appear to be a simple problem to solve Eq. (11-1) for k as follows:

$$k = \frac{1}{a} \frac{x}{t_2 - t_1} \qquad (11\text{-}2)$$

This solution is complicated, however, by the fact that the concentration is continually changing, being a at t_1 but $(a - x)$ at t_2. Therefore, Eq. (11-2) gives only an approximate value for k, since it assumes that the concentration remains constant at the value a throughout the time interval $t_2 - t_1$. The expression for the exact value of k may be found, through the application of the calculus, to be

$$k = \frac{2.303}{t_2 - t_1} \log \frac{a}{a - x} \qquad (11\text{-}3)$$

When t_1 equals zero, Eq. (11-3) reduces to the form

$$k = \frac{2.303}{t} \log \frac{a}{a - x} \qquad (11\text{-}4)$$

in which a represents the original concentration of the reacting substance and $(a - x)$ represents its concentration at the end of time t.

Half-period. The *half-period*, or *period of half-life*, of a reaction is the time required for 50 per cent of the substance present at the beginning of the period to be transformed. It is indicated by the symbol $t_{1/2}$. At this point the value of $a/(a - x)$ equals 2. Substituting this value in Eq. (11-4) and solving for t gives

$$t_{1/2} = \frac{2.303}{k} \log 2 = \frac{2.303}{k} \times 0.301 = \frac{0.693}{k} \qquad (11\text{-}5)$$

[1] For gaseous reactions, a and x may be expressed as partial pressures instead of concentrations.

From Eq. (11-5) it appears that the half-period of a first-order reaction is independent of the original concentration of the reacting substance. This is characteristic of first-order reactions and affords one means of identifying them. Another means of identifying reactions of this order depends upon the fact that a straight line is obtained when $\log (a - x)$ is plotted against t for a first-order reaction.

Example. For the reaction $Rn \rightarrow RaA + He$, the value of the velocity constant is $k = 0.1812$ when t is measured in days.

a. What is the half-period of radon?

$$t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{0.1812} = 3.82 \text{ days}$$

b. How long will it take for a sample of radon to be 80 per cent decomposed? That is, if $a = 1$, when will $x = 0.8$? From Eq. (11-4) we find that

$$0.1812 = \frac{2.303}{t} \log \frac{1}{1 - 0.8}$$

from which

$$t = \frac{2.303}{0.1812} \log 5.0 = \frac{2.303}{0.1812} \times 0.699 = 8.88 \text{ days}$$

The hydrolysis of ethyl acetate

$$C_2H_5CH_3CO_2 + H_2O \rightarrow C_2H_5OH + HCH_3CO_2$$
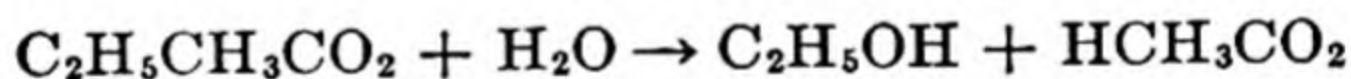
when carried on in the presence of a large excess of water is a first-order reaction. To make this reaction proceed with a reasonable speed, a small concentration of hydronium ion is added as a catalyst. The course of the reaction may be followed by withdrawing small portions of the reaction mixture and determining the amount of acetic acid formed. This determination may be done by titration with a standard solution of a base. The results of such an experiment are given in Table 11-1. In this table the figures in the first column represent the number of minutes that the reaction has been going on, the figures in the second column represent the number of milliliters of standard sodium hydroxide solution required to neutralize 10 ml. of the reaction mixture, and the figures in the third column represent values that are proportional to x, the number of moles per liter of the ester that have been transformed.

It is assumed that the reaction is complete when t equals

TABLE 11-1. DATA ON THE HYDROLYSIS OF ETHYL ACETATE

t, min.	Sodium hydroxide, ml.	x
0.0	0.95	0.00
14.0	1.87	0.92
34.0	3.09	2.14
199.0	9.77	8.82
539.0	14.04	13.09
Infinity	15.06	14.11

infinity. The amount of base, 0.95 ml., required to neutralize 10 ml. of the reaction mixture when t equals zero is a measure of the amount of hydronium ion added as a catalyst. This amount must be subtracted from all subsequent readings to determine the amount of base used to neutralize the acetic acid formed by the hydrolysis. It is in this way that the figures in the third column are obtained. These values are proportional to x, the amount of ester transformed. When the reaction is complete, $x = a$; therefore 14.11 is proportional to a, the amount of ester originally present.[1]

From these data we may calculate the velocity constant as follows:

$$k = \frac{2.303}{14} \log \frac{14.11}{14.11 - 0.92} = 0.1645 \log 1.07 = 0.00484$$

The student should calculate the velocity constant from the data for some other value of t. He should also calculate the half-period for the reaction (*Ans.* $t_{\frac{1}{2}} = 143$ min.) and, by plotting $\log (a - x)$ against t, should show that this is a first-order reaction.

Another well-known first-order reaction is the inversion of sucrose,

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$
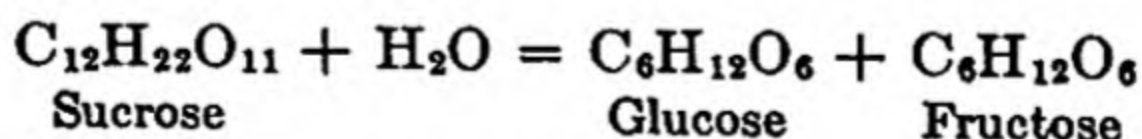
[1] Since, in the term $a/(a - x)$ of Eq. (11-4), the units used in the numerator and denominator cancel out, the value of k is independent of the units used for expressing concentrations. We do not, therefore, need to express x and a in moles per liter, but may use any convenient units. The value of k is, however, dependent on the units used to express t.

This reaction is catalyzed by hydronium ion. The course of the reaction may be followed by taking advantage of the fact that, while sucrose rotates the plane of polarized light in a clockwise direction (dextrorotatory), the mixture of glucose and fructose rotates it in the opposite direction (levorotatory). This change in rotation may be followed by means of the polarimeter.

Second-order Reactions. For a second-order reaction the law of mass action may be stated algebraically as

$$\frac{x}{t_2 - t_1} = kab \tag{11-6}$$

in which a and b represent the concentration of the two reacting substances and x represents the change in concentration of each substance during the brief interval $t_2 - t_1$. In this case, k has the dimensions of $1/(\text{concentration} \times \text{time})$, and its physical significance cannot be stated so simply as was possible in the case of the first-order reaction.

Application of the calculus will give the following expression for the velocity constant of a second-order reaction:

$$k = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)} \tag{11-7}$$

In the special case when $a = b$, this simplifies to

$$k = \frac{x}{ta(a - x)} \tag{11-8}*$$

From Eq. (11-8) the student can readily derive an expression for the half-period, when equivalent quantities of the two reactants are present, *i.e.*, when $a = b$.

$$t_{\frac{1}{2}} = \frac{1}{ka} \tag{11-9}$$

From Eq. (11-9) it appears that, when the reactants are present in equal concentrations, the half-period of a second-order reaction is inversely proportional to the concentration of the reactants. Another means of identifying reactions of this order

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* Note that this equation involves $x/a(a - x)$. In this case the units used in the numerator and denominator do not cancel out. Therefore the value of k is dependent on the units in which concentrations are expressed. It is customary to express x and a in moles per liter for solutes and in partial pressures for gases.

depends upon the fact that a straight line is obtained when $1/(a - x)$ is plotted against t.

Table 11-2 shows the data for a typical second-order reaction, the saponification of ethyl acetate,

$$C_2H_5CH_3CO_2 + OH^- \rightarrow C_2H_5OH + CH_3CO_2^-$$
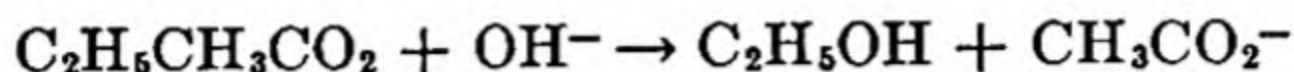
The initial concentration of the ester and of the hydroxide ion was each 0.01 molar. In this case the course of the reaction may be followed by measuring the decrease in the concentration of hydroxide ion, either by titration with a standard solution of an acid or by measuring the resulting decrease in the conductance of the solution.

TABLE 11-2. DATA ON THE SAPONIFICATION OF ETHYL ACETATE

t min.	x moles per liter
0.0	0.00000
5.0	0.00245
7.0	0.00313
9.0	0.00367
11.0	0.00414
13.0	0.00459
15.0	0.00496
18.0	0.00540
20.0	0.00566
Infinity	0.01000

From the data in Table 11-2, we may calculate the value of the velocity constant for the reaction as follows:

$$k = \frac{x}{ta(a - x)} = \frac{0.00245}{5.0 \times 0.01 \times (0.01 - 0.00245)} = 6.49$$

From this value for the velocity constant, we may calculate the half-period for the reaction as follows:

$$t_{\frac{1}{2}} = \frac{1}{ka} = \frac{1}{6.49 \times 0.01} = 15.4 \text{ min.}$$

The student should show, by plotting $1/(a - x)$ against t, that this is a second-order reaction.

Reactions of Higher Orders. Reactions of the third or higher order are rare. Reactions of the third order may be identified by the fact that if the reactants are present in equivalent amounts the plot of $1/(a - x)^2$ against t produces a straight line.

Determination of the Order of a Reaction. The various methods for determining the order of a reaction can be summarized as follows:

1. *Trial Method.* A reaction can be identified as first or second order by obtaining experimental data at different times during the reaction and substituting these data in Eqs. (11-4) and (11-7) or (11-8). That equation which gives the most nearly constant value for k identifies the order of the reaction.

2. *Graphical Method.* If the initial concentrations of the reactants are equal, a straight line will be obtained from the following plots:

First Order.   Plot $\log (a - x)$ against t.
Second Order.   Plot $1/(a - x)$ against t.
Third Order.   Plot $1/(a - x)^2$ against t.

3. *Half-period Method.* If the initial concentrations of the reactants are equal, the half-period is related to the initial concentration as follows:

First Order.   Half-period is independent of a.
Second Order.   Half-period is proportional to $1/a$.
Third Order.   Half-period is proportional to $1/a^2$.

Temperature and Reaction Velocity. A rise in temperature almost invariably increases the speed of a chemical reaction. For many reactions occurring near room temperature the speed is doubled or trebled for a 10°C. rise.

On the basis of experiment Arrhenius found that the following equation expressed the relation between temperature changes and changes in the velocity constant for a reaction:

$$\log \frac{k_2}{k_1} = \frac{A}{2.303R} \left(\frac{T_2 - T_1}{T_2 T_1} \right) \qquad (11\text{-}10)$$

In Eq. (11-10) k_1 and k_2 are the values of the velocity constant at the absolute temperatures T_1 and T_2, R is the gas constant, and A is a constant characteristic of the reaction. The constant A has the dimensions of energy and must be expressed in units consistent with those in which R is expressed.

The significance of the constant A is that it represents the *energy of activation* of the molecules of the reactants.

Activated Molecules. It will be recalled from the discussion in Chap. 7 on chemical equilibrium that in order for a reaction to occur between two molecules they must possess a certain

minimum energy at the moment they come in contact with each other.

The *average energy* of the molecules of a substance is a function of the temperature, but the energy of individual molecules may vary widely from the average value. As a result of collisions between molecules some may acquire momentarily an energy considerably in excess of the average energy. Those molecules which possess sufficient energy so that they will react upon contact are said to be *activated*. Ordinarily only a very small fraction of the molecules of a substance possesses this requisite energy, *i.e.*, is activated. The concentration of activated molecules is one of the factors affecting the speed of a reaction.

If the energy of activation is large, only a small fraction of the molecules will possess the necessary excess energy to react, and hence the reaction will be slow. If, however, the energy of activation is small, a greater number of molecules will possess the necessary energy, and the reaction will be rapid.

The concentration of activated molecules can be increased by increasing the fraction of all the molecules that possess the necessary minimum energy. This can be done by adding energy (usually in the form of heat) to the substance. The amount of energy that would have to be added to raise the average energy of all the molecules to the average energy of the activated molecules is known as the *energy of activation* of the reactants in a reaction and corresponds to A in Eq. (11-10).

The concentration of activated molecules can also be increased by increasing the concentration of all the molecules, since, at constant temperature, a constant fraction of all the molecules possesses the necessary minimum energy.

The speed of the reaction can likewise be increased if some way can be found to decrease the energy of activation necessary for a particular reaction, for in this case, at a given temperature, a greater fraction of the molecules will possess the energy needed to meet this lowered requirement. This lowering of the energy of activation for a particular reaction is the function of a *catalyst*.

CATALYSIS

A *catalyst* may be defined as a substance that alters the speed of a chemical reaction but may itself be recovered unchanged at the end of the reaction. Positive catalysts increase the speed of a reaction; negative catalysts decrease it. Both types are

known and are of great importance. An example of a positive catalyst is the finely divided iron used to catalyze the union of hydrogen and nitrogen in the Haber process for the preparation of ammonia. Examples of negative catalysts are the antioxidants added to rubber to inhibit its deterioration and thus prolong its life.

It is believed that catalysts cannot initiate a reaction, but merely alter the speed of one that already is going on. However, when the speed in the absence of the catalyst is infinitely slow, it can be said that, for all practical purposes, the catalyst makes the reaction possible. Since the catalyst is recovered unchanged at the end of the reaction, we conclude that it has contributed no energy to the reaction. It is found that the catalyst does not shift the equilibrium point of the reaction, but merely changes the speed with which the equilibrium point is reached. From this it follows that the catalyst must affect the speeds of the forward and reverse reactions to the same extent.

Homogeneous Catalysts. When the reactants and the catalyst form a single phase, the catalyst is said to be a *homogeneous* one. To this class belong the hydronium ion, which catalyzes the hydrolysis of ethyl acetate, and the iodide ion, which catalyzes the decomposition of hydrogen peroxide. The experiment with methylene blue described in the preceding chapter is another example of a homogeneous catalyst, for a small amount of the dye increases the rate at which glucose is oxidized by dissolved oxygen.

It is believed that substances that serve as positive catalysts in homogeneous systems do so by lowering the energy of activation for the reaction. They do this by forming an intermediate compound with a reactant, this intermediate compound either decomposing spontaneously or reacting with another substance to produce the desired final product. Thus, two or more consecutive reactions are substituted for the original one, the catalyst being regenerated at the end of the series. If the energy of activation of these successive reactions is less than that for the original reaction they will proceed more rapidly.

Consider, for example, the reaction $A + B \rightarrow D$, which has a high energy of activation and is, consequently, slow. Upon introduction of the catalyst C, we may have an intermediate reaction $A + C \rightarrow AC$, which has a low energy of activation and

hence is rapid. This is followed by a second reaction AC + B → D + C, which likewise has a low energy of activation and is rapid. As a result of these two reactions the speed of formation of D from A and B is increased, and the catalyst is recovered unchanged at the end of the reaction. The action of nitric oxide as a catalyst for the oxidation of sulfur dioxide in the lead-chamber process for making sulfuric acid is an example of this type of action.

Heterogeneous Catalysts. When the catalyst forms a separate phase from the reactants, it is said to be a *heterogeneous* catalyst. Examples of this are the manganese dioxide or ferric oxide used to catalyze the decomposition of potassium chlorate, also the platinum used to catalyze the union of sulfur dioxide and oxygen in the contact process for making sulfuric acid. The following experiment provides a convenient demonstration of heterogeneous catalysis. In a small Erlenmeyer flask put some methyl alcohol. Bubble air through this, and, while the air is bubbling, suspend in the neck of the flask a spiral of fine platinum wire, or a piece of platinum gauze, which has been heated. The platinum catalyzes the reaction

$$2CH_3OH + O_2 \rightarrow 2HCHO + 2H_2O$$
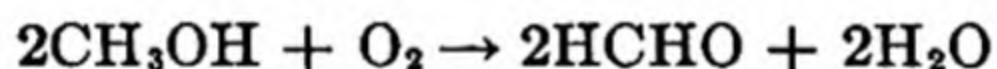
Since the reaction is exothermic the platinum will become red-hot and, if the air is bubbled through at the proper rate, the temperature becomes high enough to ignite the alcohol-air mixture, resulting in a small explosion.

The explanation usually advanced to account for heterogeneous catalysis states that the catalyst adsorbs the reactants on its surface. If a strong force of attraction exists between the surface of the catalyst and some part of the adsorbed reactant, this may cause a loosening of bonds elsewhere in the reacting molecule, and this may result in a decrease in the energy of activation for the reaction. This will cause an increase in the speed of the reaction. If the products are less strongly adsorbed than the reactants, they will be released from the surface of the catalyst, thus leaving it free for further action. In this case it would appear that the speed of a reaction catalyzed by a given mass of catalyst will depend upon the surface area of the catalyst. This is in agreement with the fact that the efficiency of a catalyst increases with its degree of subdivision, since this increases its

surface area. We should expect that substances in the colloidal state, since they have an enormous surface area per unit mass, would be very efficient catalysts. This frequently proves to be the case.

Autocatalysis. When pure nitric acid is added to copper, the reaction between the two substances proceeds slowly at first, but very soon increases markedly in speed. This increase in speed is caused by the catalytic action of the nitrous acid that is formed in the course of the reaction. This phenomenon of a reaction producing its own catalyst is known as *autocatalysis*.

Catalytic Poisons. The action of many catalysts is inhibited by the presence of other substances. When this happens the catalyst is said to be *poisoned*. It will be remembered that minute traces of arsenic poisoned the platinum used in the contact process and stimulated the search for another catalyst that would not suffer from this defect.

A possible explanation of the way in which these poisons for heterogeneous catalysts act is that they are adsorbed on the surface of the catalyst more strongly than are the reactants. Thus the reactants are prevented from coming in contact with the catalyst. Poisons for homogeneous catalysts may react with them in such a way as to prevent their forming intermediate compounds with the reactants.

Enzymes. Many life processes are dependent upon the presence of organic catalytic agents which are known as *enzymes* (from the Greek words meaning "in yeast"). These are substances that are produced by the living cell. They are essential for making the food we eat, and the oxygen we breathe, available in a form that the body can use for energy and growth. A typical example is *amylase*, which catalyzes the hydrolysis of starch to maltose.

The number and complexity of the enzymes render any discussion of them beyond the scope of this text. The present evidence indicates that they are heterogeneous catalysts and are protein in nature. Each enzyme has a definite pH at which it functions most efficiently. The efficiency of the enzyme decreases rapidly as the pH varies on either side of the optimum value.

The Kinetics of Catalyzed Reactions. One of the characteristics of the catalyst is that small quantities of it are capable of catalyzing the reaction between relatively enormous quantities

of the reactants. These reactants upon which the catalyst acts are known as the *substrate*. The velocity of the reaction is dependent not only upon the concentration of the substrate, but upon the concentration of the catalyst as well. For example, in the hydrolysis of ethyl acetate, if the concentration of the ester is held constant, the speed of the reaction varies with the concentration of the hydronium ion that catalyzes it. This fact has been used as the basis of a method for the determination of moderately large concentrations of hydronium ion.

The ability of a small amount of catalyst to act upon a large amount of substrate is found in the heterogeneous catalysts, as well as in the homogeneous ones. This is to be expected if our concept of the mechanism of heterogeneous catalysis is correct. For if the products of the reaction are released from the surface of the catalyst, this becomes free to adsorb more substrate and catalyze its reaction. There is a limit, however, to the amount of substrate that a given amount of catalyst can handle in unit time. For example, the inversion of sucrose is catalyzed by the enzyme invertase. If a fixed amount of the enzyme is taken, it is found that the velocity of the reaction increases with increasing concentration of the substrate, but only up to a certain point. If the concentration of sucrose is increased beyond this, the velocity of the reaction remains constant. Apparently the catalyst is working at the limit of its capacity, and the fact that more substrate is available does not increase the ability of the catalyst to handle it. The addition of more enzyme would, however, increase the rate of the reaction.

The Effect of Temperature. An increase in temperature increases the speed of catalyzed reactions as well as those which take place without catalysts. But, in the case of enzyme-catalyzed reactions, it is found that there is an optimum temperature for the reaction. Temperature rises above this result in a decrease in reaction velocity. A possible explanation for this is that the higher temperature destroys the enzyme.

ADSORPTION

Adsorption is defined as a *change in concentration at an interface*. If the concentration increases, the adsorption is *positive;* if the concentration decreases, the adsorption is *negative*. The following experiments will serve to demonstrate adsorption.

A eudiometer tube is filled with gaseous ammonia over mercury. If now a small amount of activated coconut charcoal is inserted in the tube, the mercury will rise, indicating a decrease in the pressure of the ammonia. It is believed that this results from the concentration of the ammonia on the surface of the charcoal, *i.e.*, at the interface between the solid and gaseous phases. This is positive adsorption.

Add about 0.01 g. of Congo red (or methylene blue) to 100 ml. of water. Add to this about 2.0 g. of decolorizing carbon and shake well. Upon filtering the mixture, the filtrate will be found to be decolorized. The dye has become concentrated on the surface of the carbon, *i.e.*, at the interface between the solid and liquid phases. This is another example of positive adsorption. It should be noted that, in this case, there are three components involved: (1) the solid adsorbent, carbon; (2) the solute, Congo red, which is adsorbed; and (3) the solvent, water. In this case it is the *solute* which is concentrated on the surface of the adsorbent. A few cases are known in which the *solvent* is adsorbed. This causes a *decrease* in the concentration of the *solute* at the interface. This is known as *negative* adsorption.

The preceding examples illustrate the two main types of adsorption, *viz.*, gases on solids and solutes on solids. We shall consider these more in detail and investigate their probable causes.

Adsorption of Gases on Solids. The adsorption of gases on solids exhibits certain characteristics that should be noted.

1. The amount of gas adsorbed per unit weight of adsorbent increases as the concentration, or partial pressure, of the gas increases. However, the adsorbent will eventually become saturated, and beyond this point further increases in the concentration of the gas will not increase the amount of adsorption.

2. Adsorption is a reversible process, so that if the pressure of the gas is decreased there will be a release of adsorbed gas. This indicates that an equilibrium exists between the adsorbed and unadsorbed gas. The establishment of equilibrium may be prevented, however, by complicating chemical reactions. For example, charcoal may not only adsorb a gas, but may also act as a reducing agent for the gas, thus preventing the attainment of an equilibrium concentration of the gas on the charcoal.

3. The degree of adsorption decreases as the temperature rises. Gases that are well above their critical temperatures are adsorbed very poorly. Gases that are near, or below, their critical temperatures are adsorbed well, and the lower the temperature, the greater the degree of adsorption. Thus, at room temperature, oxygen (critical temperature −119°C.) is adsorbed to a negligible extent by charcoal, while ammonia (critical temperature +132° C.) and many of the war gases are strongly adsorbed. Advantage is taken of this fact in the use of charcoal in the gas mask.

4. The adsorption of gases is a very rapid process. It is estimated that the air passing through a gas mask is cleansed of its adsorbable impurities in 0.01 sec.

5. The extent of adsorption depends not only upon the surface area of the adsorbent, but also upon its chemical nature and previous history. Thus charcoal that has been activated by being heated under pressure in a current of steam is a more efficient adsorbent than untreated charcoal. Silica gel is also used as an adsorbent for gases.

The Freundlich Adsorption Isotherm. When an adsorption experiment is carried out at constant temperature, the plot of the data obtained is known as an *isotherm*. Table 11-3 gives some data for the adsorption of carbon dioxide on wood charcoal at 293°K.

TABLE 11-3. ADSORPTION OF CARBON DIOXIDE ON WOOD CHARCOAL AT 293°K.

p	$\log p$	x	x/m	$\log x/m$
2.0	0.3010	14.4	4.859	0.6856
2.9	0.4624	19.5	6.579	0.8181
6.3	0.7993	38.0	12.82	1.1079
8.5	0.9294	46.4	15.65	1.1945
12.8	1.1072	62.3	21.02	1.3226
18.6	1.2695	77.5	26.15	1.4174
28.8	1.4594	94.5	31.88	1.5035
37.4	1.5729	113.2	38.19	1.5820
50.0	1.6990	131.2	44.26	1.6460

In Table 11-3, m represents the mass of charcoal used. In this experiment, $m = 2.964$ g. The symbol p represents the partial pressure of carbon dioxide, expressed in centimeters of mercury,

and x represents the volume, reduced to standard conditions, of carbon dioxide adsorbed on the charcoal. This volume is expressed in cubic centimeters.

In Fig. 11-1 is shown the isotherm obtained by plotting x/m against p. Various empirical equations to fit this curve have
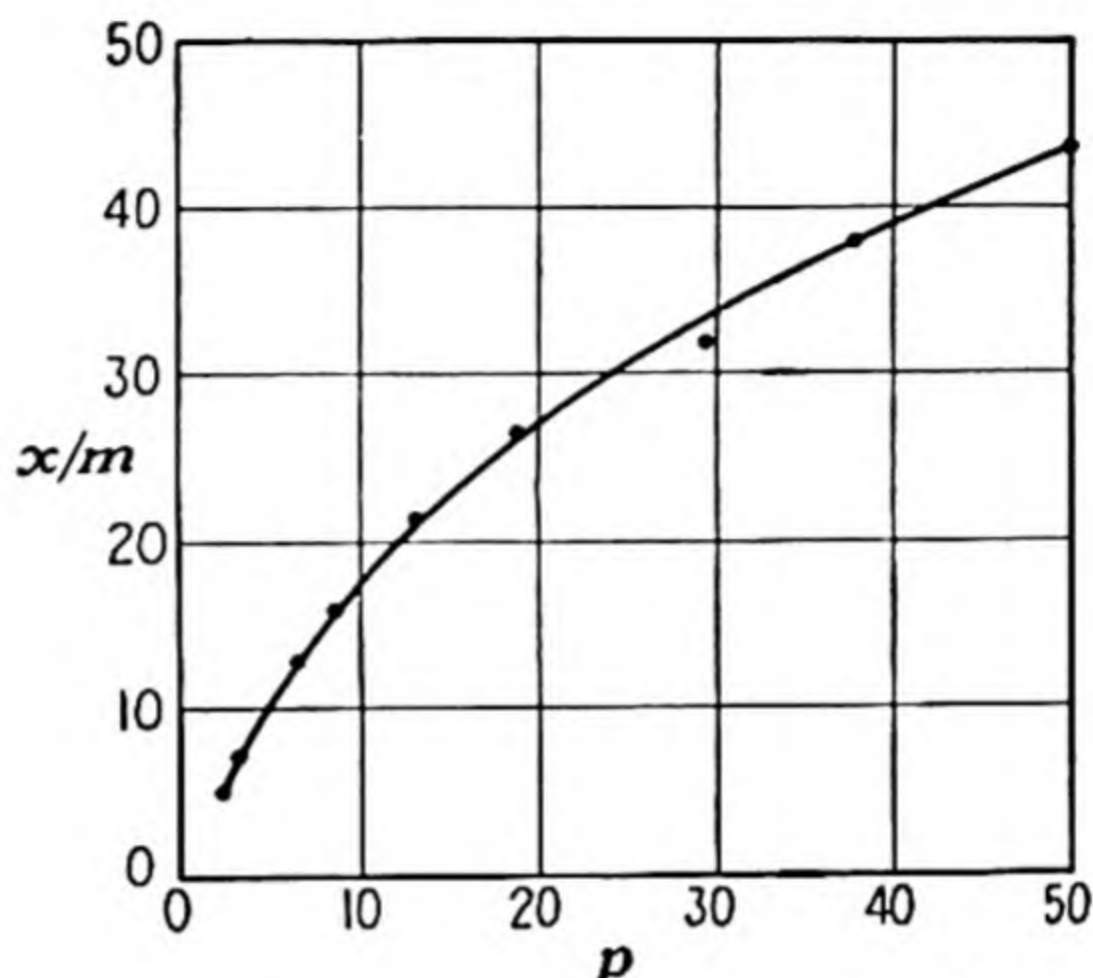
FIG. 11-1. Isotherm for the adsorption of carbon dioxide on wood charcoal at 293°K. From the data in Table 11-3.

been suggested. One of the first of these was that proposed by Freundlich,

$$\frac{x}{m} = ap^b \tag{11-11}$$

In Eq. (11-11), x represents the volume of gas adsorbed, m represents the mass of the adsorbent, and p represents the partial pressure of the gas, while a and b are constants. With the proper values of a and b, this equation fits the experimental curve fairly well, at least up to the point at which the adsorbent becomes saturated and the curve flattens out.[1] The approxi-

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[1] An alternative equation is the one proposed by Langmuir,

$$\frac{x}{m} = \frac{k_1 p}{1 + k_2 p}$$

in which k_1 and k_2 are constants, while x, m, and p have the same significance that they did in Eq. (11-11). This equation fits the experimental data somewhat better than does the Freundlich equation, particularly at higher pressures where the adsorbent is approaching saturation.

mate values of a and b for any particular system may be determined as follows. Take the logarithm of each side of Eq. (11-11). This gives

$$\log \frac{x}{m} = \log a + b \log p \qquad (11\text{-}12)$$

The plot of $\log x/m$ against $\log p$ approximates a straight line, this being a characteristic of gaseous adsorptions. Figure 11-2 shows the line obtained by plotting $\log x/m$ against $\log p$ from the data in Table 11-3. The value of $\log a$ is given by the intercept of the line with the vertical axis, where $\log p = 0.0$. The
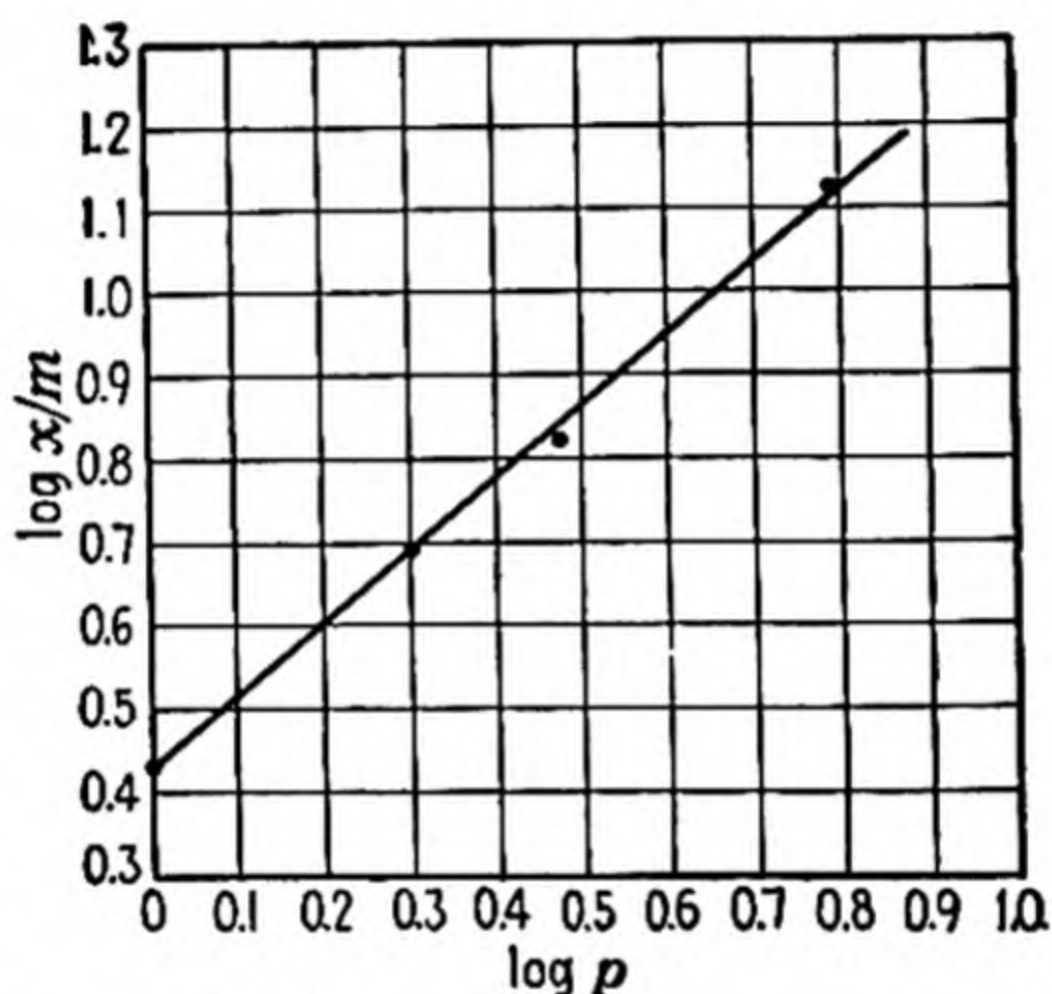
FIG. 11-2. Log x/m plotted against log p. From the data in Table 11-3.

value of b is given by the slope of the line. From this we find that $\log a = 0.43$, $a = 2.69$, and $b = 0.845$. The value of a varies with the units in which x, m, and p are expressed. The value of b is less than 1.0, but approaches unity as the temperature rises.

Two types of forces may be operative in producing the adsorption of gases on solids. The first type, which predominates at low temperatures, consists of the van der Waals forces which exist between the molecules of the gas. The degree of adsorption due to these forces closely parallels the ease of liquefaction of the gas. This type of adsorption is characterized by a small heat of adsorption and by the rapid attainment of equilibrium following changes of temperature and pressure.

The second type, which may appear at higher temperatures, consists of the formation of covalent bonds between the gas molecules and the surface of the adsorbent. For example, when oxygen is adsorbed on charcoal and is then driven off, the *desorbed* gas is found to contain some carbon monoxide and carbon dioxide. This type of adsorption is characterized by a large heat of adsorption and by failure to establish equilibrium rapidly following changes in temperature and pressure.

Adsorption of Solutes on Solids. Adsorption on solid surfaces may also take place from solutions. Either of the components of the solution may be adsorbed, but adsorption of the solvent is ordinarily very limited in extent. We shall consider only the adsorption of solutes. Examples of this type may be grouped into two classes, depending upon the probable mechanism of the adsorption.

Adsorption Caused by Changes in Surface Tension. The reader will recall the statement of the Gibbs theorem made in the discussion of surface tension: *Those substances that lower the surface tension tend to become concentrated at the interface.* According to this theorem, if a solute lowers the surface tension between water and charcoal, the solute will be concentrated at the charcoal-water interface. In other words, the solute will be positively adsorbed. This is sometimes called *mechanical adsorption.* There are many examples of this type of adsorption. They show the following general characteristics:

1. The amount of solute adsorbed per unit weight of adsorbent depends upon the concentration of the solute, but once the adsorbent has become saturated, further increases in the concentration of the solute will not result in increased adsorption.

2. The adsorption is reversible, but this fact may be concealed by chemical changes resulting from the adsorption. Thus, egg albumin adsorbed upon charcoal becomes coagulated and can then no longer be removed simply by dilution of the solution.

3. The adsorption isotherm is fitted by an equation similar to that applied to the isotherm for gaseous adsorption. This equation is

$$\frac{x}{m} = aC^b \tag{11-13}$$

In Eq. (11-13), x represents the amount of solute adsorbed, m

represents the mass of the adsorbent, C represents the concentration of the solute in the solution, and a and b are constants.

4. A given substance is more strongly adsorbed from a solvent of high surface tension than it is from one of low surface tension. Thus, picric acid is strongly adsorbed on charcoal from water solution but only slightly from alcohol solution. This affords one means of removing an adsorbed substance from the adsorbent, *viz.*, by washing it with a solvent having a lower surface tension than that from which the original adsorption was made. Thus, picric acid adsorbed on charcoal from water may be removed by washing with alcohol. This removal of an adsorbed substance is known as *elution*.

5. An adsorbed substance may be displaced from the surface of the adsorbent by another substance that is more strongly adsorbed. This affords a second means of elution. For example, in the isolation of vitamin B_1 from its natural sources, the vitamin was adsorbed on fuller's earth from an acid solution. The fuller's earth was then suspended in a solution of quinine sulfate. The quinine sulfate was more strongly adsorbed and thus caused the elution of the vitamin.

Adsorption Caused by Electrostatic Forces. Many solids, when brought in contact with water, acquire an electrical charge. For example, silica in contact with water becomes negatively charged, the water being positively charged. An experimental demonstration of this will be described in the next chapter. This charge may be caused by the selective adsorption of hydroxide ions on the surface of the solid, the ions being attracted by the unsatisfied surface valences of the solid. The solid, now bearing a charge, will adsorb any oppositely charged particles that may also be present in the water. This type of adsorption is known as *electrostatic adsorption*. It is independent of the effect of the adsorbed substance on the surface tension of the solvent. However, both types of adsorption may be operative in the same system.

Electrostatic adsorption may be demonstrated as follows. To 500 ml. of boiling water, add concentrated ferric chloride solution, a drop at a time, with constant stirring, until the mixture turns a clear deep-red color. Allow the mixture to cool. The red color is due to the presence of positively charged

particles of hydrated ferric oxide, which have been produced by the hydrolysis of the ferric chloride. To 100 ml. of this mixture, add 30 g. of powdered silica, shake for 1 min., and then filter. The filtrate will be colorless, the positively charged particles of ferric oxide having been adsorbed by the negatively charged silica. To observe the effect of silica upon negatively charged particles, proceed as follows. Prepare a saturated solution of arsenious oxide by boiling a small amount of the solid with 250 ml. of water. Filter off the excess solid, and cool the solution. Saturate a separate 250-ml. portion of water with hydrogen sulfide. Upon adding the two solutions to each other, a clear yellow mixture will be produced, whose color is due to the presence of negatively charged particles of arsenious sulfide. To 100 ml. of this mixture, add 30 g. of powdered silica, shake for 1 min., and then filter. The filtrate still retains its yellow color, for the negatively charged arsenious sulfide is not adsorbed by the similarly charged silica.

The use of sand filter beds in the purification of municipal water supplies depends upon the ability of the sand to remove, by adsorption, bacteria and other suspended impurities in the water.

Problems

1. The half-period for the decomposition of radium B is 26.8 min. Calculate the value of the velocity constant for the decomposition.

2. A first-order reaction is 15 per cent complete at the end of 20 min. How long will it take for the reaction to be 75 per cent complete?

3. If the initial concentrations of each of the reactants is 0.1 molar, a second-order reaction is 12 per cent complete in 30 min.

   a. Calculate the value of the velocity constant for the reaction.

   b. Calculate the half-period for the reaction.

   c. How long would it take for the reaction to be 35 per cent complete if the initial concentration of each of the reactants was 0.03 molar?

4. For the decomposition of nitrogen pentoxide the value of the velocity constant, at 0°C., is 7.3×10^{-7}. At 50°C. the value of the velocity constant is 8.7×10^{-4}. What is the energy of activation for the decomposition of nitrogen pentoxide?

5. The decomposition of hydrogen peroxide when catalyzed by iodide ion was measured by Harned [*J. Am. Chem. Soc.*, **40**, 1461 (1918)]. The reaction is $2H_2O_2 \rightarrow 2H_2O + O_2$. The course of the reaction may be followed by measuring the volume of oxygen released. The milliliters of oxygen released are proportional to x, the moles per liter of hydrogen peroxide transformed. The following table lists some of Harned's data.

t, min.	Oxygen, ml.
0.0	0.0
5.0	10.10
10.0	18.20
15.0	24.90
20.0	30.30
30.0	38.20
40.0	43.60
50.0	47.05
60.0	49.40
Infinity	53.90

Identify the order of the reaction, and calculate the value of the velocity constant.

6. Freundlich gives the following data for the adsorption of acetic acid on blood charcoal. C represents the concentration of acetic acid in moles per liter, and x/m represents the millimoles of acid adsorbed per gram of charcoal. The temperature of the experiment is not specified.

C	x/m
0.0181	0.467
0.0309	0.624
0.0616	0.801
0.1259	1.11
0.2677	1.55
0.4711	2.04
0.8817	2.48
2.785	3.76

Determine the values of the constants a and b to be used in Eq. (11-13) for this adsorption.

CHAPTER 12

THE COLLOIDAL STATE. THE DONNAN EQUILIBRIUM

The Colloidal State

When sand is shaken with water, the resulting mixture is known as a *suspension*. Such a suspension possesses certain characteristics, some of which may be attributed to the size of the particles of the sand. These particles are large enough to be seen, either with the naked eye or with the aid of a microscope; the mixture is obviously heterogeneous. Because of their size, the sand particles may be separated from the water, either by letting them settle under the influence of gravity or by filtration. On the other hand, when sugar is shaken with water, the resulting mixture is called a *solution*. Certain of the properties of a solution may be attributed to the size of the solute particles. We believe that these particles are of the size of small molecules or of ions. They are too small to be seen by any means now at our disposal. Therefore the mixture appears homogeneous. The solute cannot be separated by settling or by filtration.

If we start with particles the size of those found in a suspension and continuously subdivide them until their size becomes that of particles in a solution, we find that the properties of the mixture of the particles with water change continuously from the properties of a suspension to those of a solution. In the course of this transition from suspension to solution, the mixture passes through an intermediate state that partakes of the properties of each. This is known as the *colloidal state*. Many of the properties of the colloidal state may be attributed to the size of the particles in it. These particles, while too small to be seen even with a microscope, are believed to be giant molecules or aggregates of small molecules and are larger than the particles in a solution. Although it is impossible to set arbitrary limits to the particle sizes found in the colloidal state, it is usually considered that particles whose size is greater than 0.1 μ belong in the class of suspensions, those whose size is less than 1.0 mμ

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belong in the class of solutions, while intermediate sizes are to be classed as colloids.[1]

Because of this small particle size, colloidal mixtures frequently appear homogeneous to the naked eye, although their heterogeneity may be demonstrated by appropriate means. The particles will not settle out under the force of gravity, nor may they be separated by ordinary filtration. However, they will settle under the enhanced gravitational force produced in a centrifuge, and they may be separated by special forms of filtration.

Two things should always be kept in mind concerning the colloidal state. (1) The term does not apply to a particular class of substances, but is a state that any substance may be made to assume by using appropriate methods. (2) It is impossible to draw any sharp boundaries separating the colloidal state from suspensions and from solutions. The properties of one state shade gradually into those of the other.

This indefiniteness as to exactly what constitutes the colloidal state makes it difficult to formulate a definition of it. The reader may wish to use the following one as a starting point for formulating his own. *The colloidal state is a heterogeneous dispersion of two immiscible phases, which is more or less permanent, and possesses certain distinguishing characteristics.* Table 12-1 lists some of these distinguishing characteristics. They will be discussed in the succeeding sections.

From Table 12-1 it appears that in some respects colloids resemble suspensions and in other respects they resemble solutions. This should indicate the impossibility of drawing definite boundaries between the three states.

Probably all body fluids are to be considered as examples of the colloidal state. Blood is a colloid. Many foods, *e.g.*, milk, are colloids. In fact the colloidal state is encountered so universally that the study of it constitutes a large and vital branch of chemistry. All that we can hope to do in this chapter is to explain the terms used in describing colloids and to discuss briefly their means of preparation and their properties.

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[1] $1\,\mu = 1$ micron $= 1 \times 10^{-3}$ mm. $= 1 \times 10^{-6}$ m.

$1\,m\mu = 1$ millimicron $= 1 \times 10^{-6}$ mm. $= 1 \times 10^{-9}$ m.

$1\,\mu\mu = 1$ micromicron $= 1 \times 10^{-9}$ mm. $= 1 \times 10^{-12}$ m.

TABLE 12-1. CHARACTERISTICS THAT DISTINGUISH COLLOIDS FROM SUSPENSIONS AND SOLUTIONS*

	Suspension	Colloid	Solution
Particle size	$> 0.1\mu$	$0.1\mu - 1\ m\mu$	$< 1\ m\mu$
Filtration:			
Ordinary	Separated by	Not separated	Not separated
Ultra	Separated by	Separated by	Not separated?
Settling:			
Under gravity	Settles	Does not settle	Does not settle
Centrifuge	Settles	Settles	Does not settle?
Appearance	Opaque	Clear?	Clear
Tyndall cone	Shows	Shows?	Does not show?
Diffusion	Does not	Very slow	Rapid
Brownian movement	May show	Shows	Not observable

* The interrogation points in Table 12-1 mean that the particular characteristic may or may not be shown depending upon the composition of the mixture and the mechanism or technique used to observe it. For a discussion of this, see the section on some of the distinguishing characteristics of the colloidal state.

The Phases of a Colloid. Of the two phases that constitute a colloid we usually say that one is scattered, or dispersed, in the other. The phase that is scattered is variously called the *dispersed phase*, the *internal phase*, or the *discontinuous phase*. This phase usually forms the smaller fraction of the colloid. The phase in which the scattering is done is called the *dispersion medium*, the *external phase*, or the *continuous phase*. This phase usually forms the larger fraction of the colloid.

TABLE 12-2. DIFFERENT TYPES OF COLLOIDAL DISPERSIONS

Dispersed phase	Dispersion medium	Example
Solid—gold	Solid—glass	Ruby glass
Solid—gold	Liquid—water	Gold sol
Solid—fine ash	Gas—air	Smoke
Liquid—water	Solid—silica	Opal
Liquid—fat	Liquid—water	Milk
Liquid—water	Gas—air	Fog
Gas—air	Solid—silicates	Pumice
Gas—air	Liquid—water	Foam

Each of the phases that make up a colloid may be chosen from any of the three states of matter—solid, liquid, gas—with the single exception that the two phases cannot both be gases. Two gases are completely miscible and always form a true solution. Table 12-2 lists examples of colloids composed of the other possible combinations.

Sols and Gels. When a colloid presents the fluid appearance of a solution, it is termed a *sol*. Sols are quite frequently named according to the nature of the dispersion medium. Thus a *hydrosol* is one whose external phase is water. One whose continuous phase is alcohol is called an *alcosol*. Smoke is an *aerosol*. Colloids whose structure is more rigid than that of a sol are called *gels*. The degree of rigidity may vary from that of thin jellies to that of structures such as horn. Certain colloids, such as gelatin in water, may occur as either sols or gels. At high temperatures and low concentrations of gelatin, the mixture is a hydrosol with the gelatin as the dispersed phase. As the concentration of gelatin is increased and the mixture is cooled, the colloid assumes the form of a gel. It is believed that this transformation is the result of a *reversal* of the phases. The gelatin particles imbibe water and swell until they touch each other. The gelatin is now the continuous phase, forming a lattice, the interstices of which contain water as the internal phase. Heating, or the addition of more water, will once more reverse the phases and restore the colloid to the sol form.

Suspensoid. Emulsoid. Sols in which the dispersed phase has little affinity for the dispersion medium are called *suspensoids*. Sols in which the dispersed phase has a considerable affinity for the dispersion medium are called *emulsoids*. Among the hydrosols, colloidal gold is an example of a suspensoid. The gold has a negligible affinity for water, and the colloid is termed a *hydrophobic* one. On the other hand, gelatin has a great affinity for water and is highly hydrated. Gelatin and water produce an emulsoid. This is also called a *hydrophilic* colloid. Table 12-3 lists some of the characteristics that serve to distinguish suspensoids from emulsoids.

The term "reversibility" used in Table 12-3 may refer to two different phenomena. It may refer to the ability of a colloid in the gel form to reverse its phases and become a sol. We have seen that gelatin is capable of doing this and is, therefore, con-

sidered to be reversible.   On the other hand, colloidal silicic acid will change readily from the sol to the gel form, but once the gel is formed it is not possible to get it to change back to the sol form.   Silicic acid is irreversible.   The term "reversibility" may also refer to the ability to restore the substances to the colloidal state simply by mixing the two phases after they have been separated.   Thus, when the two phases of a gelatin hydrosol are

TABLE 12-3.   CHARACTERISTICS DISTINGUISHING SUSPENSOIDS AND EMULSOIDS

	Hydrosols	
	Suspensoids hydrophobic	Emulsoids hydrophilic
Dispersed phase...........	Inorganic substances Metals Sulfides Oxides	Organic substances Starch Proteins Albumin Gelatin
Maximum concentration of dispersed phase..........	Low	High
Viscosity..................	About the same as water	Greater than water
Surface tension............	About the same as water	Lower than water
Preparation...............	Difficult	Easy
Precipitation..............	Easy	Difficult
Reversibility..............	Irreversible	Reversible

separated, the colloidal state may be restored simply by mixing the water and the gelatin.   This colloid is reversible.   On the other hand, when the two phases of a gold hydrosol are separated, the colloidal state cannot be restored simply by bringing the gold in contact with water.   This colloid is irreversible.   For either meaning of the term it can, in general, be said that hydrophilic colloids are reversible, while hydrophobic ones are irreversible.

The Preparation of Hydrosols.   The preparation of two typical hydrosols, hydrated ferric oxide and arsenious sulfide, was described at the end of Chap. 11.   Other preparations that can conveniently be used for demonstrations are the following:

1. *Gold by Tannic Acid.* To 250 ml. of distilled water, add a few drops of a solution of gold chloride; then add a few milliliters of a solution of tannic acid. The auric ions are reduced to metallic gold which appears in the colloidal form. The solution gradually turns red, the depth of color depending upon the amount of gold present. Impure reagents may produce an unstable blue sol.

2. *Gold by Bredig's Method.* Prepare a 0.001 molar solution of potassium chloride. Connect two gold wires, as electrodes, to the lighting circuit, in series with a resistance to prevent short circuits. The resistance should permit a current of 2 to 3 amp. Strike an arc between the electrodes under the surface of the potassium chloride solution. After a few seconds' operation of the arc, the solution will turn red from the formation of colloidal gold.

3. *Sulfur.* To a dilute solution of potassium thiosulfate, add a few drops of hydrochloric acid. In a few minutes the solution will turn opalescent, from the slow formation of colloidal sulfur.

4. *Gelatin.* Dissolve 5 g. of gelatin in 100 ml. of hot water. This forms a hydrophilic sol which, upon cooling, forms a gel.

Peptization. The term "peptization" was originally used to indicate the transformation of a gel into a sol. It has since been extended to indicate the dispersal of any solid into the colloidal form. Any substance that causes peptization is known as a *peptizing agent.* Peptizing agents may be liquids, or they may be solutes, either electrolytes or nonelectrolytes. Water is a peptizing agent for gelatin, since the simple addition of water to solid gelatin results in the formation of a sol. Many insoluble inorganic compounds may be peptized by shaking them with water containing a low concentration of one of the ions contained in the compound. Thus, pure silver chloride may be peptized by low concentrations of either silver or chloride ions. The necessary low ionic concentration may be approached from either side, *i.e.*, either by the addition of electrolyte to pure water, or by the dilution of a too concentrated solution of the electrolyte. The latter method is a frequent source of trouble in analytical chemistry. The reader will probably recall the annoying colloidal suspensions formed when the precipitated sulfides of the copper group are washed with water. The washing

reduces the concentration of hydrogen sulfide in contact with the precipitate to the point where the low concentration of sulfide ion peptizes the precipitate. To avoid this, the precipitates are washed with water containing hydrogen sulfide.

Some of the Distinguishing Characteristics of the Colloidal State. Let us consider more in detail some of the characteristics listed in Table 12-1 as distinguishing the colloidal state from suspensions and solutions.

Filtration. Colloidal particles are small enough so that they will pass through the pores of ordinary filter papers, which will prevent the passage of the particles of a suspension. However, collodion membranes can be prepared whose pores are so small that they will prevent the passage of colloidal particles, which can thus be separated from the dispersion medium. This process is known as *ultrafiltration*.

If the pores of the membrane are made sufficiently fine they may prevent the passage of large solute molecules. Thus the membranes considered in the discussion of osmotic pressure prevent the passage of molecules of sucrose, which forms a true solution in water. This emphasizes the statement that no sharp line of demarcation can be drawn between colloid and solution or suspension.

Settling. Particles of the size found in suspensions settle through water under the action of gravity more or less rapidly, depending on the size of the particle. Particles of colloidal size do not settle under the action of gravity, but will settle under the enhanced force produced in a centrifuge. Particles of molecular size will not settle under the force produced in an ordinary centrifuge, but heavy molecules, such as mercuric chloride, can be made to settle in an ultracentrifuge. Svedberg,[1] by using centrifugal forces up to 710,000 times gravity, has been able to produce settling of molecules with molecular weights as low as about 40.

Appearance. When viewed by transmitted light the colloid, depending upon the concentration of the dispersed phase, may appear opaque like a suspension or as clear as a solution. When, however, a strong narrow beam of light is passed through a colloid, which is then viewed at right angles to the beam, the path of the beam appears dusty, even though the colloid may

[1] SVEDBERG, T., *Ind. Eng. Chem., Anal. Ed.*, **10**, 118 (1938).

appear perfectly clear by transmitted light. This phenomenon is known as the *Tyndall effect*, and the dusty path of the beam is called the *Tyndall cone*. It is caused by the scattering of light by particles too small to be seen. In order for a system to show the Tyndall effect, two conditions must be satisfied.

1. The diameter of the particles of the dispersed phase must not be much smaller than the wave length of the light used.

2. The index of refraction of the dispersed phase must differ from that of the dispersion medium. This may be demonstrated by inserting a glass rod into some Canada balsam. The two substances have practically the same index of refraction; hence the rod becomes invisible where it enters the balsam.

The particles of solute in a solution are usually much smaller than the wave length of visible light. Hence true solutions ordinarily do not show the Tyndall effect. Nevertheless, as the particle size gradually increases, we may reach a point where the system, while still exhibiting some of the characteristics of a solution, now shows the Tyndall effect. On the other hand, it is possible to have colloids, particularly hydrophilic ones, in which the refractive indices of the dispersed phase and dispersion medium are so close together that the colloid does not show the Tyndall effect.

Diffusion. Dialysis. Because of their comparatively large size, the particles in a colloid have little motion of their own, while the particles in a solution, being molecular, or smaller, in size, do possess motion of their own. Hence solute particles will diffuse fairly rapidly, while the rate of diffusion of colloidal particles is negligible. This can be demonstrated by the following experiment. Fill two test tubes about half-full of a 5 per cent gelatin solution. When this has set to a jelly, pour into one test tube a little concentrated potassium dichromate solution and into the other a little ferric oxide hydrosol. In a few minutes it will be noticed that the potassium dichromate has penetrated the gelatin while the ferric oxide has not.

Advantage is taken of this difference in diffusion rates and of the inability of colloidal particles to pass through certain membranes, to separate solute particles, particularly ions, from colloidal particles by the process of *dialysis*. Figure 12-1 shows one type of dialyzer in which this can be carried on. It consists of a shallow bottomless glass dish, the opening of which is covered by

a parchment membrane. This fits into a jar containing water, so that the water touches the parchment. A mixture of a solution and a colloid is placed in the dish. The solute ions diffuse through the parchment, while the colloid particles do not. Therefore, if the water in the jar is replaced frequently to prevent the establishment of equilibrium, the colloid may be almost entirely freed of solute particles. This is known as dialysis.
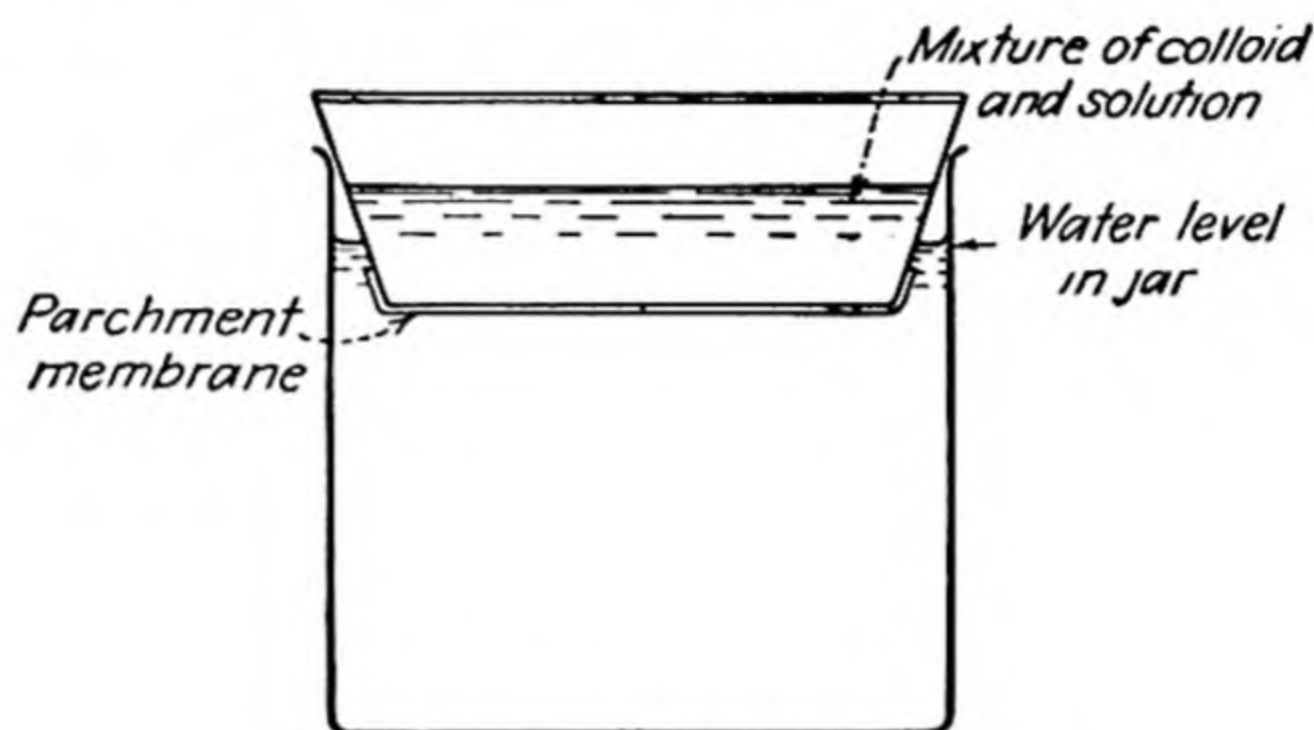
FIG. 12-1.   A dialyzer.

The Brownian Movement. Colloidal particles have little motion of their own, but the impacts of the molecules of the dispersion medium on the particles of the dispersed phase produce an erratic zigzag motion in the latter. This is known as the *Brownian movement.* It may also be observed in the particles of a suspension, provided that they are not too large. If they are too large, then the energy of the impacts of the molecules of the dispersion medium is not sufficient to produce any detectable motion. The Brownian movement in colloids may be observed by focusing a microscope on the Tyndall cone.

It will be recognized that all the characteristics just discussed are related to the size of the colloidal particle. Another important consequence of the small size of the particles is their enormous surface area. Consider a cube of matter whose edge is 1 cm. long. The surface area of this cube is 6 cm.^{2} Let this cube be subdivided into cubes of colloidal dimensions, *i.e.*, 1 mμ or 1 $\times$ 10^{-7} cm. along an edge. There will be produced 1 $\times$ 10^{21} cubes, each with a surface area of 6 $\times$ 10^{-14} cm.^{2}, or a total surface area of 6 $\times$ 10^7 cm.^{2} This is about 1.5 acres. Because of this great surface area, colloids show, to a marked degree,

those phenomena which are associated with surfaces. For example, they are frequently excellent heterogeneous catalysts.

The Electrical Properties of Colloids. The dispersed phase of a colloid bears an electrical charge. The dispersion medium bears an opposite charge. The existence of these charges may be demonstrated by the following series of experiments.
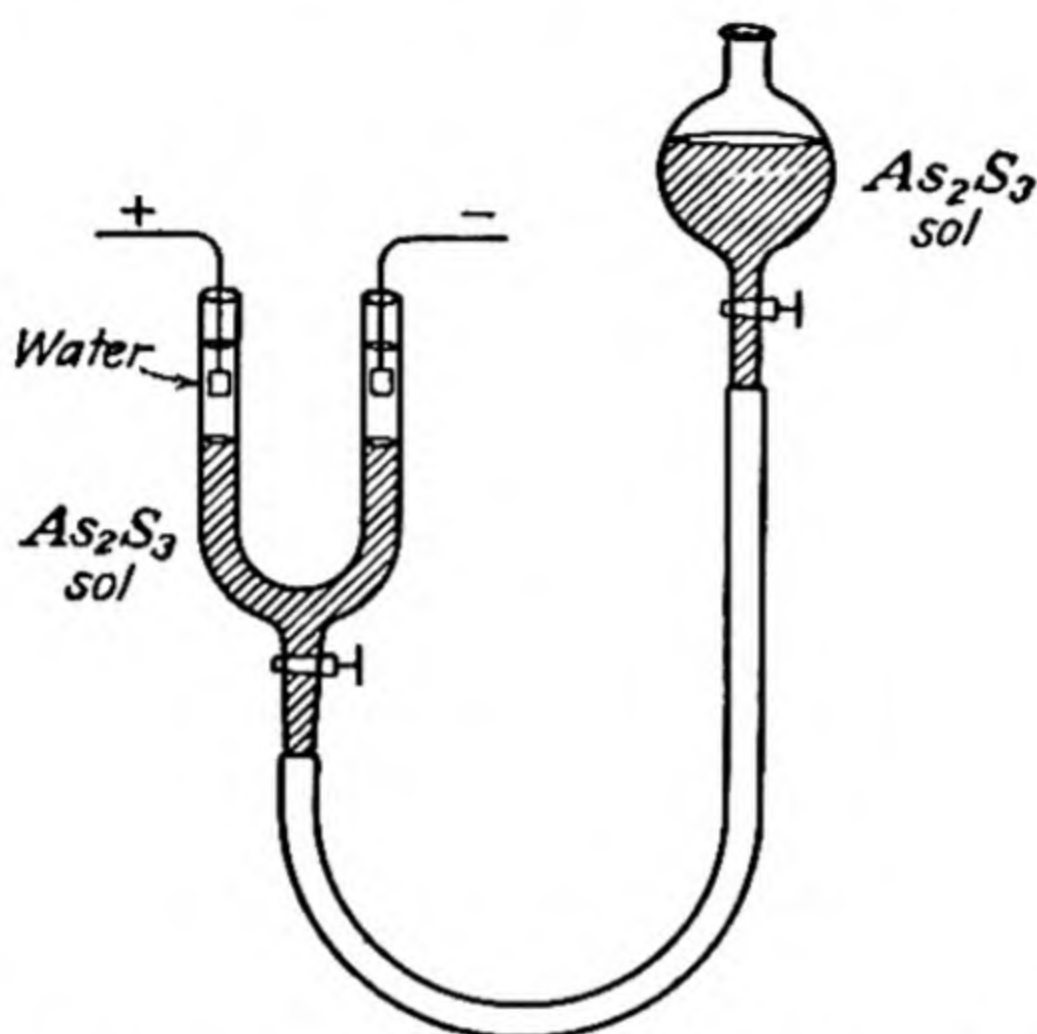
FIG. 12-2. Apparatus for demonstrating cataphoresis.

1. Set up the apparatus indicated in Fig. 12-2. Put distilled water in the U tube until it reaches about one-quarter of the way up each arm. Put an arsenious sulfide hydrosol in the dropping funnel, and allow it to flow very slowly into the U tube until the water level is raised nearly to the top of the tube. If this is done carefully, there will be a sharp boundary between the water and the sol. Insert inert electrodes in each arm, and connect to a source of direct current. (The author has used 220 volts with a lamp in series, but lesser voltages should work.) In a few minutes the arsenious sulfide is found to have moved toward the anode and away from the cathode. This indicates that the dispersed phase bears a negative charge.

This motion of the dispersed phase through the dispersion medium under the influence of an electric potential is known as *electrophoresis* or *cataphoresis*. By similar experiments we can determine the charge on other colloids. Thus colloidal gold is

found to be negatively charged, while ferric oxide is charged positively.

2. Make a U tube out of glass tubing of about 7 mm. inside diameter. Pack the bottom of the U with powdered silica, and add water until the arms of the U are about half-full. Insert an electrode into the water in each arm, and connect to a source of direct current. In a few minutes it will be observed that the water level has risen in the arm of the tube containing the cathode and has dropped in the other arm. From this we conclude that the water bears a positive charge. This flow of the dispersion medium under the influence of an electric potential is known as *electroendosmosis*.

Another simple demonstration of electroendosmosis can be performed by placing a porous plate on an iron tripod. Half fill the plate with water, and place an electrode in it. Attach the other electrode to a leg of the tripod. Connect these electrodes to a source of direct current, making the tripod the cathode. In a short time water will begin to drip from the bottom of the plate, being drawn through the plate by electroendosmosis. Reversing the current causes the water to stop dripping and the bottom of the plate to become dry.

The Precipitation of Colloids. The precipitation of substances from the colloidal state is accompanied by a coagulation or flocculation of the particles of the dispersed phase into massive particles resembling those of a suspension. These massive particles may be separated from the dispersion medium either by settling or by filtration. The precipitation of hydrophobic colloids is easier to effect than that of the hydrophilic sols. There are three principal methods by which the precipitation of hydrophobic colloids may be accomplished.

1. *Mutual Precipitation.* When two colloids, whose dispersed phases bear opposite electrical charges, are mixed in approximately equal proportions, their charges neutralize each other and both of the dispersed phases coagulate and settle out. This is known as mutual precipitation and may be demonstrated by mixing equal volumes of ferric oxide and arsenious sulfide hydrosols.

2. *Electrolysis.* If the process of cataphoresis is allowed to continue until the particles of the dispersed phase actually come in contact with the electrodes, the particles will coagulate and

precipitate, probably because the electrode has neutralized the charge on the particles. This method of breaking up a colloid has found a very useful application in the Cottrell process for precipitating the aerosol, smoke, in the chimneys of industrial plants. A wire and a plate, both highly charged, are placed in the chimney. The smoke particles assume the same charge as the wire and are then attracted to, and precipitated on, the oppositely charged plate. This not only abates the smoke nuisance, but frequently leads to the recovery of valuable by-products that more than pay for the process.

3. *The Addition of Electrolytes.* The addition of a small amount of an electrolyte, such as hydrochloric acid or salt, will cause the coagulation of ferric oxide, arsenious sulfide, or Bredig gold hydrosols. This is a general characteristic of hydrophobic colloids; they are unstable and are easily precipitated by the addition of small quantities of electrolytes. The quantity of electrolyte required to coagulate a fixed amount of colloid is a function of the valence of the ion which bears a charge opposite to that on the colloidal particle. Thus, for precipitating negatively charged arsenious sulfide it is found that divalent cations are approximately seventy times as efficient as monovalent cations, while trivalent cations are about five hundred times as effective. For precipitating positively charged suspensoids, such as ferric oxide, a similar relationship is found for the effectiveness of anions. Following the discussion of the Donnan equilibrium, we shall consider a possible explanation as to why electrolytes will precipitate colloids, and why there is a relation between valence and precipitating power.

The precipitation of emulsoids is more difficult to accomplish than is that of suspensoids. In emulsoids the dispersed phase is heavily hydrated. This degree of hydration must be greatly decreased before the colloid can be coagulated. This may be done in the following two different ways:

1. By the addition of large quantities of soluble salts. The ions of these salts become heavily hydrated and, in so doing, remove water from the dispersed phase of the colloid. This changes the nature of the colloid from an emulsoid to a suspensoid, which is then easily coagulated by the charged ions present. Those ions which are capable of being most heavily hydrated are most efficient in precipitating emulsoids.

2. By the addition of a second solvent that is miscible with water. If, for example, alcohol is added to the emulsoid, agar in water, the alcohol removes the water from the agar. The system then becomes a suspensoid and is easily precipitated by the addition of a small concentration of electrolyte.

A somewhat different procedure is effective in the case of emulsoids that are proteins. It will be recalled that proteins are ampholytes. If the pH of the dispersion medium is adjusted to a value above the isoelectric point of the protein, the latter will ionize as an acid and will form salts with the cations of the heavy metals. These salts, in general, are insoluble. Hence, if small concentrations of lead ion, silver ion, or other heavy metal ions are introduced, the protein will precipitate.

Protective Colloids. Not only are emulsoids resistant to precipitation themselves, but if they are added to suspensoids they will make the latter more difficult to coagulate. In other words, the en ulsoid *protects* the suspensoid. This is probably the result of the emulsoid forming a protective coating over the particles of the suspensoid and thus preventing their flocculation. It is probable that some of the slightly soluble components of the blood, such as calcium phosphate, are held in colloidal suspension by the protective action of the proteins in the blood.

The protective action of the spinal fluid was used by Lange as the basis of a diagnostic test for diseases such as meningitis and syphilis. Varying concentrations of the spinal fluid are added to separate portions of a specially prepared gold hydrosol. To each is then added a fixed quantity of dilute salt solution. The range of concentration of the spinal fluid through which it protects the gold sol is characteristic of the type of infection in the patient from whom the fluid was taken.[1]

Imbibition. The process by which a hydrophilic colloid becomes hydrated is sometimes termed *imbibition*. In the case of organic hydrophilic colloids, such as the proteins and starches, this hydration results in extensive swelling of the dispersed phase. The attraction of these colloids for water is so strong that imbibition and swelling will proceed even against large pressures. The pressure necessary to prevent a volume increase in such a colloid is known as the *imbibition pressure* of the colloid. This

[1] For details of the Lange test see A. W. Thomas, "Colloid Chemistry," pp. 109–110, 467–468, McGraw-Hill Book Company, Inc., New York, 1934.

quite frequently amounts to several hundred atmospheres. Imbibition pressure should not be confused with osmotic pressure. They probably result from two entirely different causes. Imbibition pressure is usually much greater than osmotic pressure and will permit a protein to remove water from salt solutions of very high osmotic pressures.

The extent of imbibition is affected by the pH of the system. Proteins show a minimum of swelling at their isoelectric point. With either increase or decrease of pH from this point, the degree of imbibition rises to a maximum at about pH = 2.5 or pH = 10.5. Hydrophilic carbohydrates, on the other hand, show their greatest amount of imbibition when the system is approximately neutral; the extent of swelling decreases as the pH either rises or falls from the neutral point.

The Nature of the Colloidal Particle. An idea of the nature of the particles present in a suspensoid may be arrived at through a consideration of certain experimental facts concerning one of the least complex of the suspensoid hydrosols—a Bredig gold sol.

1. The presence of an electrolyte is essential to the formation of the sol. Bredig gold sols will not form in distilled water. Certain specific ions are necessary to stabilize the colloid. Chloride ions and hydroxide ions will stabilize the sol. Nitrate ions will not.

2. The concentration of the stabilizing ion must be held within rather narrow limits. If the concentration of chloride ion varies much, either above or below 0.001 molar, the colloid is rendered unstable.

3. During the formation of the colloid the concentration of the stabilizing ion decreases, indicating that it is being used up in the formation of the particles of the dispersed phase. On the other hand, tests fail to reveal the presence of gold ions. Therefore it is assumed that the stabilizing ion is not combined chemically with the gold.

From a consideration of the above evidence, it is concluded that the particles of the dispersed phase consist of a variable number of neutral gold atoms grouped together with an indefinite number of chloride ions, which act as a stabilizing agent to keep the gold in the colloidal state and confer a negative charge on the particle. Such a complex particle is sometimes known as a *colloidal micelle.* A representative formula for the micelle of a

Bredig gold sol is $(Au)_x(Cl^-)_y$. The values of x and y are variable. The author has found in some cases the value 40 for the ratio x/y.

The micelles of ferric oxide and arsenious sulfide hydrosols are pictured as $(Fe_2O_3)_x(H_2O)_y(Fe^{+++})_z$ and $(As_2S_3)_x(S^{--})_y$. The stabilizing ion confers the charge on the particle. In combination with the Donnan equilibrium, this concept of the colloidal particle will be used in a possible explanation of the precipitating action of electrolytes on suspensoids.

The particles of emulsoids are undoubtedly more complex than those of suspensoids. We shall make no attempt in this text to picture their nature.

The Donnan Equilibrium

The principle known as the Donnan equilibrium is applicable to a situation that is very frequently encountered in physiology. Living systems are, of course, much more complicated than the exceedingly simple ones we shall use in our discussion and are not susceptible of a simple mathematical treatment. Nevertheless, an understanding of the simple systems will help us to understand why the living systems behave as they do.

Consider a system made up of the following components:

1. A water solution of an electrolyte, one of whose ions is small enough to be diffusible, the other ion being so large as to approach colloidal dimensions and to be nondiffusible. A familiar example of such a *colloidal electrolyte* is Congo red, having the following formula:

$$C_6H_4N_2C_{10}H_5(SO_3H)NH_2$$
$$|$$
$$C_6H_4N_2C_{10}H_5(SO_3)NH_2Na$$
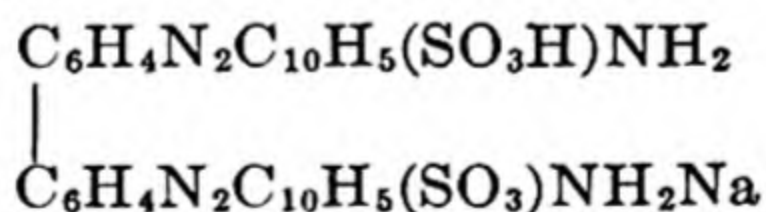
This ionizes to furnish the diffusible cation, Na^+, and the nondiffusible dye anion. We shall designate this solution as the internal solution.

2. A water solution of an electrolyte, both of whose ions are diffusible. We shall designate this solution as the external one.

3. A semipermeable membrane separating the two solutions, the membrane being permeable to all ions except the nondiffusible one.

In such a system the diffusible ions will move across the

membrane until equilibrium is established. The principle enunciated by Donnan is that at equilibrium the products of the concentrations of the pairs of diffusible ions going to make up any possible electrolyte will be equal on the two sides of the membrane.

We shall consider three different types of situations in which the Donnan equilibrium is operative. These are as follows:

Case I. The electrolytes in the internal and external solutions have an ion in common.

Case II. The electrolytes in the internal and external solutions have no ion in common.

Case III. The external liquid contains no solute, but is simply water.

To simplify the mathematics as much as possible, we shall make the following restrictions:

1. All ions shall be monovalent.

2. The volumes of the internal and external solutions shall be equal to each other.

3. There shall be no volume change in either solution; *i.e.*, there shall be no shift of solvent.

With these restrictions in mind we can derive expressions for the conditions obtaining at equilibrium in each of the three cases mentioned above.

Case I. The electrolytes in the internal and external solutions have an ion in common. Let us represent the initial conditions in this case as follows:

$$\begin{array}{cc|cc} \mathrm{Na^+} & \mathrm{R^-} & \mathrm{Na^+} & \mathrm{Cl^-} \\ c_1 & c_1 & c_2 & c_2 \end{array}$$
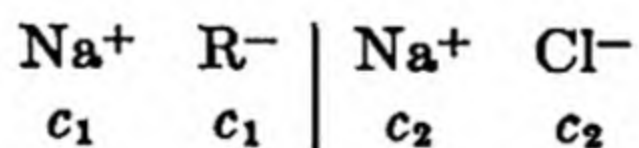
In the above expression, $\mathrm{R^-}$ represents the nondiffusible anion, c_1 represents the concentration of the electrolyte in the internal solution, and c_2 represents the concentration of the electrolyte in the external solution. Note that c_1 always refers to the concentration of the colloidal electrolyte, *i.e.*, the one furnishing the nondiffusible ion. The vertical line represents the semipermeable membrane.

Since the internal solution contains no chloride ions, some will diffuse into it from the external solution. Let x represent the moles per liter of chloride ion which so move. The two solutions must at all times be electrically neutral, and this means that x

moles/liter of sodium ion must also diffuse from the external to the internal solution. Therefore, at equilibrium the conditions are

$$\begin{array}{ccc|cc} \text{Na}^+ & \text{R}^- & \text{Cl}^- & \text{Na}^+ & \text{Cl}^- \\ (c_1 + x) & c_1 & x & (c_2 - x) & (c_2 - x) \end{array}$$
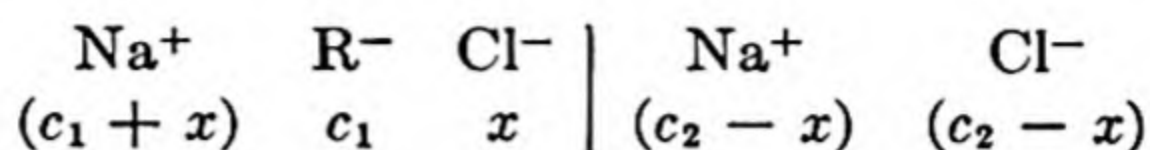
The Donnan equilibrium requires that, at equilibrium,

$$[\text{Na}^+][\text{Cl}^-] = [\text{Na}^+][\text{Cl}^-] \qquad (12\text{-}1)$$
$$\underset{\text{Internal}}{} \qquad \underset{\text{External}}{}$$

Substituting for the concentrations of the substances in Eq. (12-1) their equivalents in terms of c_1, c_2, and x gives

$$(c_1 + x)x = (c_2 - x)^2$$

This expression may be solved for x to give

$$x = \frac{c_2{}^2}{c_1 + 2c_2} \qquad (12\text{-}2)$$

From Eq. (12-1) we can derive another important relationship, *viz.*,

$$\frac{[\text{Na}^+]_{\text{internal}}}{[\text{Na}^+]_{\text{external}}} = \frac{[\text{Cl}^-]_{\text{external}}}{[\text{Cl}^-]_{\text{internal}}} = r \qquad (12\text{-}3)$$

An expression for calculating the value of the ratio r can be derived as follows:

$$r = \frac{[\text{Cl}^-]_{\text{external}}}{[\text{Cl}^-]_{\text{internal}}} = \frac{(c_2 - x)}{x}$$

By substituting in this expression the value of x found in Eq. (12-2), we obtain the following expression for the ratio r:

$$r = \frac{c_1 + c_2}{c_2} \qquad (12\text{-}4)$$

From Eq. (12-4) it appears that, for a fixed value of c_1, as the value of c_2 increases the value of r approaches unity.

At this point the student should derive the similar set of expressions for the colloidal electrolyte RCl which furnishes the non-diffusible cation R^+. He will find that the value of x is still given by Eq. (12-2) but that the value of r given by Eq. (12-4) is in this case for the ratio

$$r = \frac{[\text{Na}^+]_{\text{external}}}{[\text{Na}^+]_{\text{internal}}} = \frac{[\text{Cl}^-]_{\text{internal}}}{[\text{Cl}^-]_{\text{external}}} \qquad (12\text{-}5)$$

In other words, if we consider the ions bearing charges of the same sign as those on the nondiffusible ions, then the value for the ratio r given by Eq. (12-4) is always for the expression

$$r = \frac{\text{concentration of ion in external solution}}{\text{concentration of ion in internal solution}}$$

Example 1. If the initial concentrations are as represented below, calculate the equilibrium concentrations and the value of the ratio r.

$$\begin{array}{cc|cc} \text{Na}^+ & \text{R}^- & \text{Na}^+ & \text{Cl}^- \\ 0.1 & 0.1 & 0.1 & 0.1 \end{array}$$

$$x = \frac{c_2^2}{c_1 + 2c_2} = \frac{0.1^2}{0.1 + 0.2} = \frac{0.01}{0.3} = 0.033$$

Therefore, at equilibrium, the following conditions obtain:

$$\begin{array}{ccc|cc} \text{Na}^+ & \text{R}^- & \text{Cl}^- & \text{Na}^+ & \text{Cl}^- \\ 0.133 & 0.1 & 0.033 & 0.067 & 0.067 \end{array}$$

The value of the ratio r is

$$r = \frac{[\text{Na}^+]_{\text{internal}}}{[\text{Na}^+]_{\text{external}}} = \frac{c_1 + c_2}{c_2} = \frac{0.1 + 0.1}{0.1} = 2.0$$

Example 2. If the initial concentrations are as represented below, calculate the equilibrium concentrations and the value of the ratio r.

$$\begin{array}{cc|cc} \text{R}^+ & \text{Cl}^- & \text{Na}^+ & \text{Cl}^- \\ 0.1 & 0.1 & 0.5 & 0.5 \end{array}$$

$$x = \frac{c_2^2}{c_1 + 2c_2} = \frac{0.5^2}{0.1 + 1.0} = \frac{0.25}{1.1} = 0.227$$

Therefore, the equilibrium concentrations are

$$\begin{array}{ccc|cc} \text{Na}^+ & \text{R}^+ & \text{Cl}^- & \text{Na}^+ & \text{Cl}^- \\ 0.227 & 0.1 & 0.327 & 0.273 & 0.273 \end{array}$$

The value of the ratio r is

$$r = \frac{[\text{Na}^+]_{\text{external}}}{[\text{Na}^+]_{\text{internal}}} = \frac{c_1 + c_2}{c_2} = \frac{0.1 + 0.5}{0.5} = \frac{0.6}{0.5} = 1.2$$

Certain facts should be noted concerning the equilibriums illustrated above.

1. The presence of the nondiffusible ions causes an unequal distribution of the diffusible ions between the two solutions. At equilibrium, the sum of the concentrations of the diffusible ions in the internal solution is greater than the sum of the concentrations of the same ions in the external solution.

2. The total concentration of ions is greater in the internal solution than in the external one. Thus the internal solution has a higher osmotic pressure than the external one.

3. The osmotic pressure of the internal solution with respect to the external one is determined not only by the concentration of the nondiffusible ions, but also by the greater concentration of the diffusible ions caused by the establishment of the Donnan equilibrium. Therefore, measurements of osmotic pressure between the two solutions cannot be used to determine the concentration of the nondiffusible ion, unless the difference in the concentrations of the diffusible ions is eliminated or allowed for. The difference in the concentrations of the diffusible ions may be practically eliminated by increasing the value of c_2 until the value of the ratio r approaches unity. Then the osmotic pressure between the two solutions is due almost entirely to the concentration of the nondiffusible ion.

Case II. The electrolytes in the internal and external solutions have no ion in common. Let the initial conditions in this case be represented as follows:

$$\begin{array}{cc|cc} Na^+ & R^- & K^+ & Cl^- \\ c_1 & c_1 & c_2 & c_2 \end{array}$$
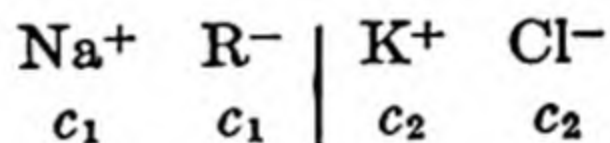
This case differs from the preceding one in that there are three kinds of diffusible ions rather than two. Let x represent the amount moved of that ion of the external solution that is opposite in charge to the nondiffusible ion. In this case, x represents the number of moles per liter of potassium ion which migrate. Let z represent the number of moles per liter of the diffusible ion of the internal solution that move. In this case, z refers to the sodium ion. Let y represent the amount moved of that ion of the external solution that has the same charge as the nondiffusible ion. In this case, y refers to the chloride ion. From the requirement that the two solutions shall remain electrically neutral, we find that

$$z = x - y \tag{12-6}$$

When equilibrium is attained, the concentrations will be

$$\begin{array}{cccc|ccc} Na^+ & R^- & K^+ & Cl^- & Na^+ & K^+ & Cl^- \\ (c_1 - z) & c_1 & x & y & z & (c_2 - x) & (c_2 - y) \end{array}$$
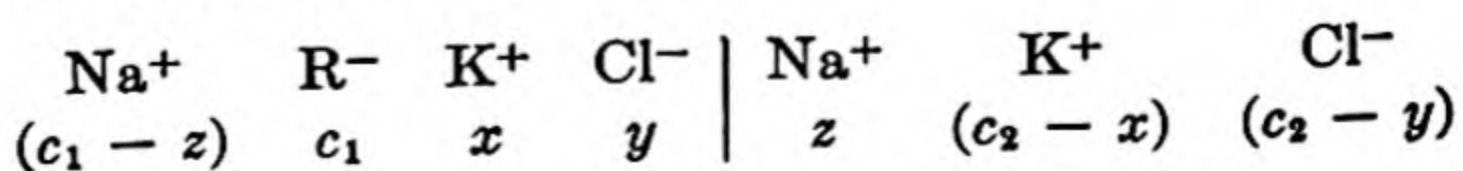
The Donnan principle requires that at equilibrium the following two equations must be satisfied:

$$[Na^+][Cl^-] = [Na^+][Cl^-] \qquad (12\text{-}7)$$
$$\underset{\text{Internal}}{} \qquad \underset{\text{External}}{}$$

and

$$[K^+][Cl^-] = [K^+][Cl^-] \qquad (12\text{-}8)$$
$$\underset{\text{Internal}}{} \qquad \underset{\text{External}}{}$$

Substituting for the concentrations in Eq. (12-7) their equivalents in terms of c_1, c_2, x, y, and z gives

$$(c_1 - z)y = z(c_2 - y)$$

or

$$(c_1 - x + y)y = (x - y)(c_2 - y)$$

from which we find that

$$x = \frac{y(c_1 + c_2)}{c_2} \qquad (12\text{-}9)$$

Using the same procedure with Eq. (12-8), we find that

$$xy = (c_2 - x)(c_2 - y)$$

from which we find that

$$x = c_2 - y \qquad (12\text{-}10)$$

If now we equate the expressions for x given in Eqs. (12-9) and (12-10), we obtain

$$\frac{y(c_1 + c_2)}{c_2} = c_2 - y$$

from which we find that

$$y = \frac{c_2{}^2}{c_1 + 2c_2} \qquad (12\text{-}11)$$

Once the value of y has been determined, the value of x may be calculated by use of Eq. (12-10) and then the value of z can be obtained by use of Eq. (12-6).

From Eqs. (12-7) and (12-8) we may derive the following relationship:

$$\frac{[Na^+]_{\text{internal}}}{[Na^+]_{\text{external}}} = \frac{[K^+]_{\text{internal}}}{[K^+]_{\text{external}}} = \frac{[Cl^-]_{\text{external}}}{[Cl^-]_{\text{internal}}} = r \qquad (12\text{-}12)$$

An expression for calculating the value of the ratio r can be derived as follows:

$$r = \frac{[\text{Cl}^-]_{\text{external}}}{[\text{Cl}^-]_{\text{internal}}} = \frac{c_2 - y}{y}$$

By substituting in this expression the value of y given by Eq. (12-11), we can obtain the following expression for the ratio r:

$$r = \frac{c_1 + c_2}{c_2} \tag{12-13}$$

It should be noted that the expression for r given in Eq. (12-13) is identical with that given by Eq. (12-4) for Case I. This means that in Case II also, for a fixed value of c_1, as the value of c_2 increases the value of the ratio r approaches unity.

Another important consequence is that when, in Case II, the value of c_2 is small compared with that of c_1 there will be practically complete separation of the two ions of the electrolyte in the external solution. For example, if $c_1 = 0.98$ and $c_2 = 0.01$, then at equilibrium 99 per cent of the potassium ions will have moved to the internal solution, while 99 per cent of the chloride ions will have remained in the external solution.

Example. If the initial concentrations are as represented below, calculate the equilibrium concentrations and the value of the ratio r.

Na+	R−	K+	Cl−
0.1	0.1	0.2	0.2

From Eq. (12-11) we find that

$$y = \frac{c_2^2}{c_1 + 2c_2} = \frac{0.2^2}{0.1 + 0.4} = \frac{0.04}{0.5} = 0.08$$

From Eq. (12-10) we find that

$$x = c_2 - y = 0.2 - 0.08 = 0.12$$

From Eq. (12-6) we find that

$$z = x - y = 0.12 - 0.08 = 0.04$$

Therefore, the equilibrium concentrations are

Na+	R−	K+	Cl−	Na+	K+	Cl−
0.06	0.1	0.12	0.08	0.04	0.08	0.12

The value of the ratio r is

$$r = \frac{[\text{Na}^+]_{\text{internal}}}{[\text{Na}^+]_{\text{external}}} = \frac{c_1 + c_2}{c_2} = \frac{0.1 + 0.2}{0.2} = 1.5$$

When the external solution contains divalent ions that have a charge opposite to that of the nondiffusible ion, a different set of conditions obtains at equilibrium. Consider, for example, the following initial conditions:

$$\begin{array}{cc|cc} Na^+ & R^- & Mg^{++} & Cl^- \\ c_1 & c_1 & c_2 & 2c_2 \end{array}$$
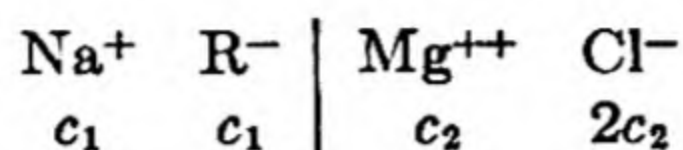
Then, at equilibrium the conditions will be

$$\begin{array}{cccc|ccc} Na^+ & R^- & Mg^{++} & Cl^- & Na^+ & Mg^{++} & Cl^- \\ (c_1 - z) & c_1 & x & y & z & (c_2 - x) & (2c_2 - y) \end{array}$$
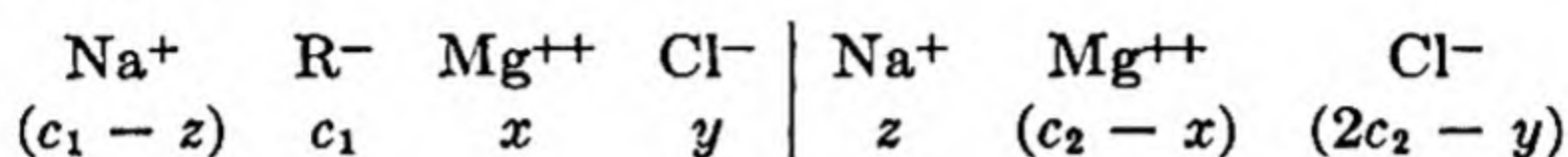
and in this case

$$z = 2x - y$$

The equilibrium requirements now are as follows:

$$\frac{[Na^+]_{internal}}{[Na^+]_{external}} = \frac{[Mg^{++}]^{1/2}_{internal}}{[Mg^{++}]^{1/2}_{external}} = \frac{[Cl^-]_{external}}{[Cl^-]_{internal}} = r \quad (12\text{-}14)$$

Attempts to solve the resulting equations for x, y, and z lead to third-degree equations of great complexity. Experiments by Loeb,[1] however, show that increases in the concentration of a divalent ion, such as magnesium ion, cause the value of r to approach unity more rapidly than do the same increases in the concentration of a monovalent ion, such as potassium ion.

Case III. The external liquid is water. Let the initial conditions be represented as follows:

$$\begin{array}{cc|c} Na^+ & R^- & H_2O \\ c_1 & c_1 & \end{array}$$
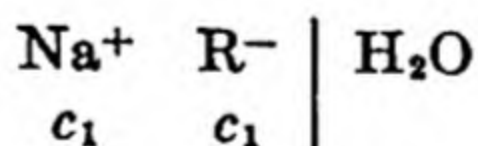
Sodium ions will move to the external solution. Let x represent the number of moles per liter of sodium ion which so move. In order to maintain electrical neutrality, an equivalent amount of hydroxide ions must also move to the external solution, leaving an equivalent excess of hydronium ions in the internal solution. The conditions at equilibrium will then be

$$\begin{array}{ccc|cc} Na^+ & H_3O^+ & R^- & Na^+ & OH^- \\ (c_1 - x) & x & c_1 & x & x \end{array}$$
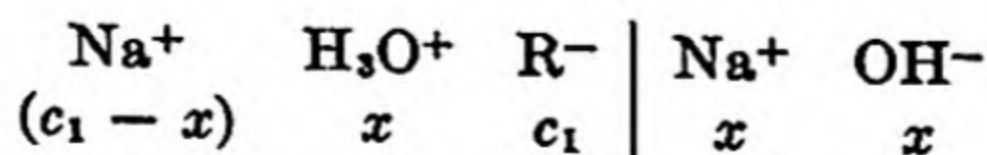
[1] LOEB, J., *J. Gen. Physiol.* **6,** 307 (1924).

The concentrations of the sodium ions and hydroxide ions must satisfy the equation

$$[Na^+][OH^-] = [Na^+][OH^-] \qquad (12\text{-}15)$$
$$\text{Internal} \qquad \text{External}$$

An approximate value for x may be obtained as follows, remembering that $[OH^-] = K_w/[H_3O^+]$. If we substitute for the concentrations in Eq. (12-15) their equivalents in terms of c_1, x, and K_w, we obtain

$$(c_1 - x)\frac{K_w}{x} = x^2$$

or

$$(c_1 - x)K_w = x^3$$

The value of x is so small compared with that of c_1 that we may assume, without introducing any considerable error, that $c_1 - x = c_1$. Therefore we can write

$$c_1 K_w = x^3$$

or

$$x = (c_1 K_w)^{\frac{1}{3}} \qquad (12\text{-}16)$$

This process of producing an excess of hydroxide ion in the external solution is sometimes known as *membrane hydrolysis*. If the nondiffusible ion is a cation, such as would be furnished by RCl, the external solution will be made acid. In this case the amounts of chloride ion and hydronium ion that move to the external solution can be calculated by means of Eq. (12-16).

Example. If the initial conditions are as represented below, calculate the equilibrium concentrations on each side of the membrane.

Na$^+$	R$^-$	H$_2$O
0.1	0.1	
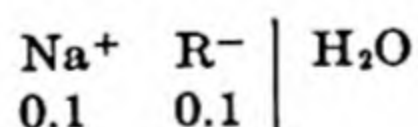
$$x = (c_1 K_w)^{\frac{1}{3}} = (0.1 \times 1 \times 10^{-14})^{\frac{1}{3}} = (1 \times 10^{-15})^{\frac{1}{3}} = 1 \times 10^{-5}$$

Therefore, at equilibrium

Na$^+$	H$_3$O$^+$	R$^-$	Na$^+$	OH$^-$
0.09999	0.00001	0.1	0.00001	0.00001
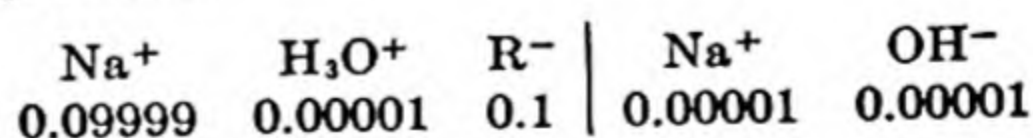
The Precipitation of Suspensoids by Electrolytes. One of the most reasonable explanations of the precipitating action of electrolytes on suspensoids is that of Wilson.[1] He assumes that,

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[1] WILSON, J. A., "The Chemistry of Leather Manufacture," 2d ed., Vol. I, pp. 171–177, *American Chemical Society Monograph* 12, Reinhold Publishing Corporation, 1928.

because of the large electrical charge on the colloidal micelle, the particle is surrounded by an atmosphere of ions of opposite charge. The concentration of the ions in this atmosphere is much greater than is the concentration of the same ions in the dispersion medium. According to this idea, the micelle of a Bredig gold sol formed in potassium chloride solution would be as represented in Fig. 12-3. The system behaves as if, in effect, it contained a membrane, on one side of which is the nondiffusible
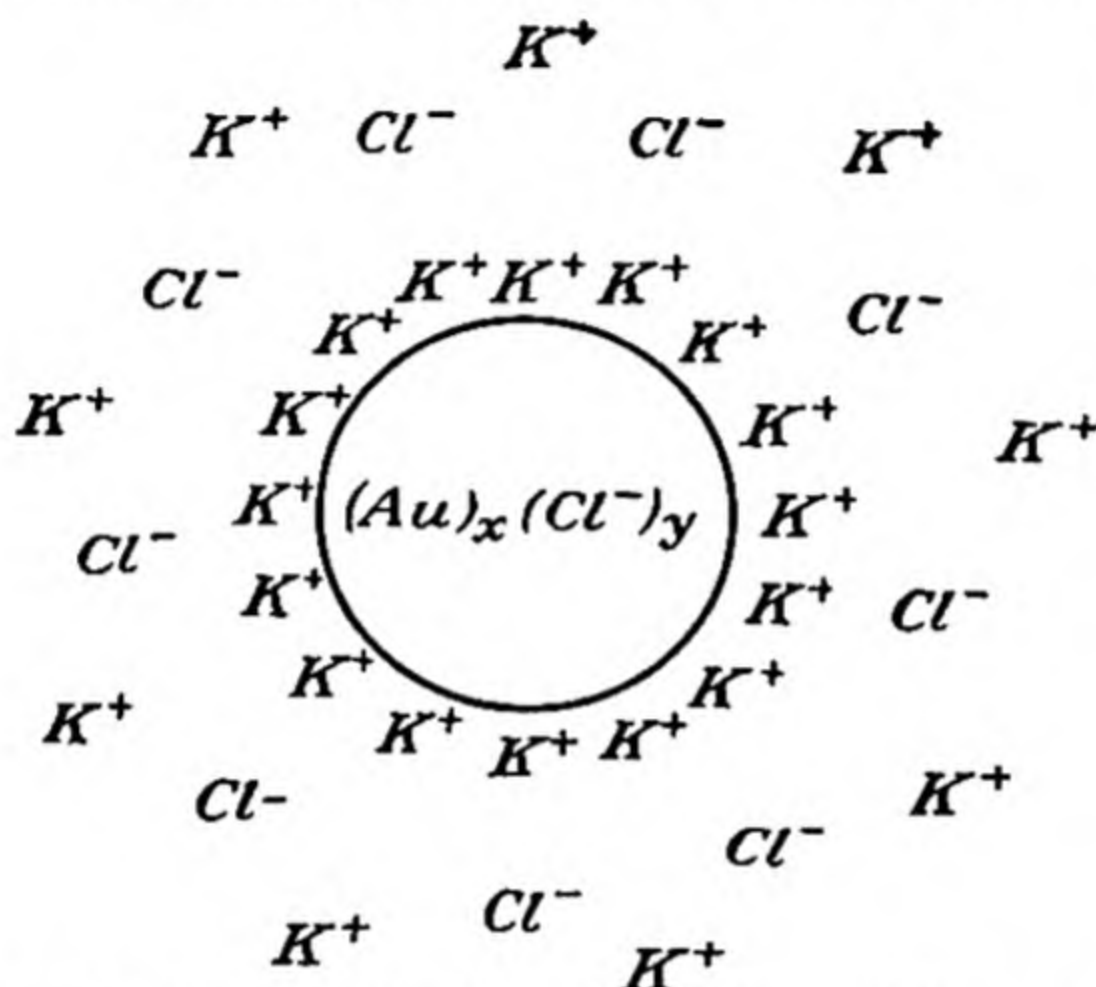
Fig. 12-3. The micelle of a Bredig gold sol formed in a potassium chloride solution.

micelle with its atmosphere of diffusible potassium ions, and on the other side are the diffusible potassium and chloride ions of the dispersion medium. In such a system, the Donnan equilibrium will be operative.

It can be shown that when a system contains two different concentrations of the same ion a potential difference exists between the parts of the system containing the different concentrations. The value of this potential, at 25°C., is given by the expression

$$E = \frac{0.059}{n} \log \frac{[\text{ion}]_1}{[\text{ion}]_2} \qquad (12\text{-}17)$$

in which n is the valence of the ion concerned. In the case of the micelle illustrated in Fig. 12-3, the potential would be

$$E = 0.059 \log \frac{[K^+]_{\text{internal}}}{[K^+]_{\text{external}}} = 0.059 \log r \qquad (12\text{-}18)$$

It is the existence of this potential that causes the particles to repel each other and prevents their coagulation. When the potential falls below a certain limiting value, the colloid becomes unstable and precipitates. According to Loeb,[1] precipitation of a hydrophobic colloid occurs when the value of E, without regard to sign, becomes less than 0.014 volt.

If the Donnan equilibrium is operative in this system, then the addition of potassium chloride, or any other electrolyte, to the dispersion medium will cause the ratio $[K^+]_{internal}/[K^+]_{external}$ to approach unity and, consequently, the value of E to approach zero. This will result in the precipitation of the colloid.

If polyvalent ions carrying a charge opposite to that on the micelle are more effective than monovalent ions in reducing the value of the ratio r and of E, we should then expect them to be more efficient as precipitating agents for suspensoids. This is a possible explanation of observed facts.

Equilibriums in the Blood. The "Chloride Shift." The blood is important as a carrier of oxygen and carbon dioxide. The amount of either one of these gases that can be dissolved in the blood is affected by the concentration of the other gas present. Oxygen is absorbed by reacting with the hemoglobin of the blood. It is believed that each complex molecule of hemoglobin (molecular weight is about 67,000) contains four atoms of iron and is capable of adding on four molecules of oxygen. The reduced hemoglobin and the oxidized hemoglobin are both acids, but the oxidized form is the stronger proton donor.

$$HHb + H_2O \rightleftharpoons H_3O^+ + Hb^- \qquad \text{reduced hemoglobin, weak acid}$$
$$+$$
$$4O_2$$
$$\Updownarrow$$
$$HHbO_8 + H_2O \rightleftharpoons H_3O^+ + HbO_8^- \qquad \text{oxyhemoglobin, stronger acid}$$
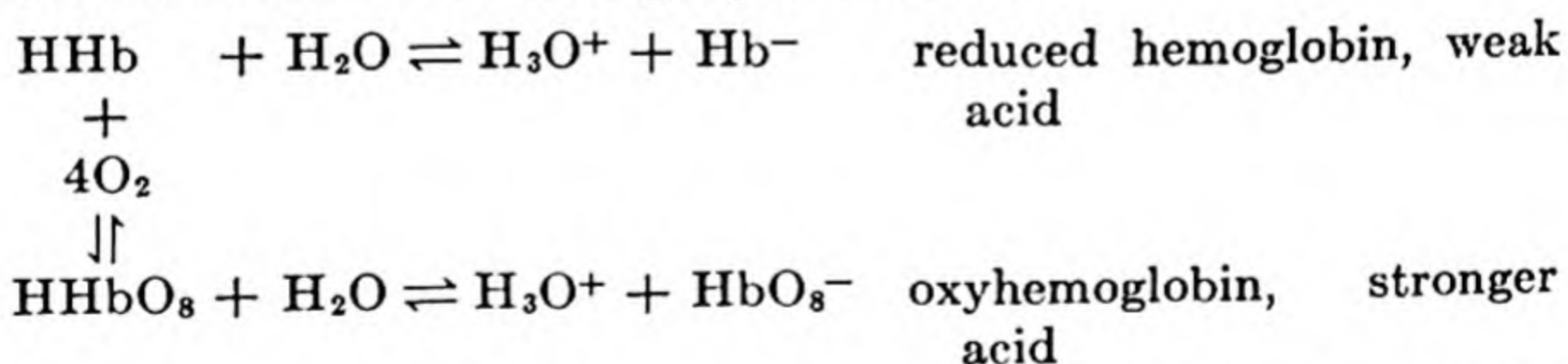
Therefore, an increase in the amount of oxygen in the blood will tend to lower its pH.

Carbon dioxide dissolves in the blood with the formation of weak carbonic acid, which ionizes to give hydronium ions and bicarbonate ions.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$
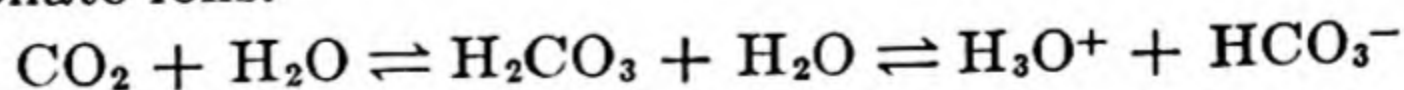
[1] Loeb, J., *J. Gen. Physiol.*, **6**, 307 (1924).

From this it appears that any decrease in the pH of the blood will drive this reaction backward and release carbon dioxide from the blood.

These reactions of oxygen and carbon dioxide with the blood may be combined into a single expression as follows:

$$4O_2 + HHb + HCO_3^- \rightleftharpoons HbO_8^- + H_2O + CO_2$$
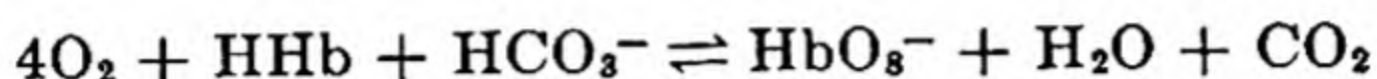
This equation expresses the experimentally demonstrable fact that, if the partial pressure of carbon dioxide is maintained constant, any increase in the partial pressure of oxygen in contact with the blood will cause a decrease in the solubility of carbon dioxide in the blood. Similarly, at a constant partial pressure of oxygen, any increase in the partial pressure of carbon dioxide will decrease the solubility of oxygen.

The reader will recall that in the discussion of viscosity it was stated that in cases of asphyxia there is an increase in the viscosity of the blood as a result of the swelling of the red corpuscles and that this swelling is caused by an increased concentration of carbon dioxide in the blood. It has also been known for a long time that changes in the partial pressure of carbon dioxide in equilibrium with the blood cause changes in the distribution of chloride and bicarbonate ions between the blood plasma and the interior of the red corpuscles. These two phenomena are interrelated and are explainable on the basis of the Donnan equilibrium.

The membrane surrounding the red corpuscle is impermeable to hemoglobin in both its oxidized and reduced forms and is also impermeable to proteins and to sodium and potassium ions. The membrane is permeable to chloride and bicarbonate ions. The interior of the corpuscle contains hemoglobin and proteins and also potassium ions, chloride ions, and bicarbonate ions. The plasma surrounding the corpuscle contains proteins and sodium ions, chloride ions, and bicarbonate ions. Thus we see that the interior of the corpuscle contains some nondiffusible ions, *viz.*, the Hb^- and HbO_8^- ions. This suggests the possibility of the establishment of a Donnan equilibrium between the external and internal solutions. In normal blood it is found that the concentration of chloride and bicarbonate ions is about twice as great in the plasma as it is in the interior of the corpuscle. In

other words, the value of the ratio,

$$r = \frac{[Cl^-]_{plasma}}{[Cl^-]_{corpuscle}} = \frac{[HCO_3^-]_{plasma}}{[HCO_3^-]_{corpuscle}}$$

is approximately 2.0.

Now assume that the partial pressure of carbon dioxide in contact with the blood is increased. This will result in a greater concentration of bicarbonate ion in the plasma. We have seen that such an increase tends to make the value of r approach unity. To accomplish this, both chloride and bicarbonate ions must move from the plasma to the interior of the corpuscle. This shift will cause an increase in the osmotic pressure of the solution inside the corpuscle, and therefore the corpuscle will swell.

A decrease in the partial pressure of carbon dioxide, or an increase in the partial pressure of oxygen, will cause a decrease in the solubility of carbon dioxide in the blood. This results in a decrease in the concentration of bicarbonate ions in the plasma, and this will cause chloride ions and bicarbonate ions to shift from the interior of the corpuscle to the plasma.

Problems

1. If the initial conditions are as represented below, calculate the equilibrium concentration of each of the diffusible ions on each side of the membrane. Calculate the value of the ratio r and also the potential, at 25°C., between the two sides of the membrane. In each case, R^+ represents a non-diffusible ion.

(a)
	Na^+	Cl^-	R^+	Cl^-
	0.6	0.6	0.2	0.2

(b)
	H_3O^+	NO_3^-	R^+	Cl^-
	0.3	0.3	0.3	0.3

2. If the initial conditions are as represented below, calculate the pH of the solution on each side of the membrane at equilibrium and also the potential, at 25°C., between the two sides of the membrane.

(a)
H_2O	Na^+	R^-
	0.8	0.8

(b)
H_2O	R^+	Cl^-
	2.7	2.7

3. A Bredig gold sol will precipitate if the concentration of potassium chloride in the dispersion medium is made 0.01 molar. Assume that at this point the potential between the micelle and the solution is 0.014 volt. Calculate the value of the ratio $[K^+]_{internal}/[K^+]_{external}$ and also the concentration of potassium ions in the ionic atmosphere surrounding the micelle.

LIST OF VISUAL MATERIALS

The following list of visual materials can be used to supplement some of the material in this book. This list, although subdivided by chapters, is a comprehensive rather than a selective list. Therefore, we would suggest that each film be previewed before using as some may contain information that is too advanced while others may contain information that is too elementary.

These films can be obtained from the producer or distributor listed with each title. (The addresses of producers and distributors are given at the end of the bibliography.) In many cases these films can be obtained from your local film library or local film distributor; also, many universities have large film libraries from which they can be borrowed.

The running time (min) and whether it is silent (si) or sound (sd) are listed with each title. All of the motion pictures are 16mm black and white films unless otherwise stated.

Each film has been listed once in connection with the chapter to which it is most applicable. However, in many cases the film might be used advantageously in other chapters.

Each of the motion pictures produced by the U.S. Office of Education has a coordinated filmstrip and an instructor's manual. In many cases, the other films have accompanying instructor's manuals.

A comprehensive list of chemistry films: "Films on Chemical Subjects," is available from the American Chemical Society, Washington 6, D.C.

CHAPTER 1—DIMENSIONS AND UNITS

Electron—An Introduction (USOE 16min sd). Explains the nature of an electron and demonstrates electronic flow by means of animated drawings.

Electrons (EBF 11min sd). Shows the flow of electrons and explains the electronic theory.

The Periodic Table (McG-H Filmstrip). Explains periodic table.

The Structure of the Atom (McG-H Filmstrip). Explains modern theory of atomic structure; such terms as nucleus, proton, neutron, electron, isotope, atomic number, mass number. Information gained from X-ray exploration of atomic and molecular crystals is summarized.

Atomic Theory (McG-H Filmstrip). Explains atomic theory and assumptions underlying it. Shows how theory helps explain related phenomena.

Elementary Electricity—Current and Electromotive Force (Castle 10min sd). Explains electron theory; discusses arrangement of molecules and building up of current, conductors, electromotive force, and resistance.

CHAPTER 2—GASES

Characteristics of Gases (EPS 9min sd). Demonstrates the physical laws governing the behavior of gases.

Molecular Theory of Matter (EBF 11min sd). The diffusion of gases and the evaporation of liquids are shown by means of animated drawings.

The Kinetic Molecular Theory (McG-H Filmstrip). Explains kinetic molecular theory; Boyle's law and Charles's law; how matter changes from one state to another.

The Chemical Formula (McG-H Filmstrip). Explanation of chemical symbols and formulas.

Equations (McG-H Filmstrip). Describes customary arrangement and meaning of equations used to summarize chemical changes and shows proper method for balancing simple equations by inspection.

CHAPTER 3—LIQUIDS

Characteristics of Liquids (BraF 11min sd). Shows the properties of liquids.

Cohesion, Invisible Forces (Coronet 5min si). Demonstrations of cohesion and surface tension.

Doctor Langmuir—on Surface Chemistry (BraF 30min sd). Doctor Langmuir performing experiments in surface chemistry.

Liquids (AFR 10min sd). Properties, such as surface tension and viscosity, of liquids.

Properties of Water (Coronet 11min sd). The chemical and physical properties of water are shown by means of experiments and demonstrations.

Surface Chemistry (B&H 30min sd). A description of oil-film experiments demonstrating size and shape of molecules.

Gravitation of Liquids (Bray 4min si). Laboratory demonstrations of specific gravity differences of liquids.

CHAPTER 5—PROPERTIES OF SOLUTIONS OF NONELECTROLYTES

Roots of Plants (EBF 11min sd). Shows growth, structure, and other characteristics of roots. Experiments in osmosis are demonstrated and explained.

CHAPTER 6—PROPERTIES OF SOLUTIONS OF ELECTROLYTES

Chemical Reactions (EPS 20min sd). Explains the composition of the atom and the relationship between nucleus and electrons.

Effects of Metallic Ions and Osmotic Disturbances on the Heart (IndU 10min sd). Effects of potassium, calcium, and sodium ions and of dehydration are demonstrated with an isolated turtle heart.

Electrochemistry (EBF 11min sd). Demonstrates the transformation of chemical energy into electrical energy and the reverse process (electrolysis).

Electrolysis (McG-H Filmstrip). Explains electrolysis and use of electrolytic principles.

Ionization (McG-H Filmstrip). Demonstrates various characteristic properties of acids, bases, and salts.

CHAPTER 8—THERMODYNAMICS

Energy and Its Transformations (EBF 11min sd). Discusses the principles of the conservation of energy and the concepts of power and work.

Thermodynamics (EBF 11min sd). Deals with heat and molecular motion, chemistry of combustion, transformation of energy, first and second laws of thermodynamics, and industrial applications.

CHAPTER 9—HYDRONIUM ION

Acid and Basic Solutions (McG-H Filmstrip). Distinct physical and chemical properties of acids and bases are demonstrated; also an explanation of pH scale is given.

CHAPTER 11—SPEED OF REACTION. CATALYSIS. ADSORPTION

Catalysis (EBF 11min sd). Shows the nature of catalytic action and indicates its importance in many chemical processes.

Velocity of Chemical Reactions (EBF 11min sd). Shows the influence of temperature on the velocity of chemical reactions; catalysts and their practical significance; reversible reactions and chemical equilibrium.

CHAPTER 12—THE COLLOIDAL STATE. THE DONNAN EQUILIBRIUM

Colloids (EBF 11min sd). Explains the characteristics of simple suspensions, emulsions, and colloids.

Colloids and Their Behavior (Rolab 20min si). Explains and demonstrates the many forms of colloids and how to produce them.

GENERAL

Energy Release from Food (Upjohn 28min sd color). Technical illustration of the chemistry involved in release of energy from food molecules.

Mechanisms of Breathing (EBF 11min sd). Shows gaseous exchange in lungs and body tissue cells. Factors affecting rate and depth of breathing.

The Slide Rule—Multiplication and Division (USOE 24min sd). Shows in detail the operation of "C" and "D" scales of the slide rule.

The Slide Rule—Percentage, Proportion, Squares, and Square Roots (USOE 21min sd). Shows how to use the "B" and "C" scales of the slide rule.

Physiology of Anoxia (Linde 23min sd). Story of breathing and blood chemistry.

SOURCES OF FILMS LISTED ABOVE

AFR—American Film Registry, 28 E. Jackson Blvd., Chicago 4, Illlinois.
B&H—United World Films Inc., 445 Park Ave., New York 22.
BraF—Brandon Films, 1600 Broadway, New York 19.
Bray—Bray Studios, Inc., 729 Seventh Ave., New York 19.
Castle—Castle Films, Inc., 445 Park Ave., New York 22.

Coronet—Coronet Instructional Films, 65 E. South Water St., Chicago 1, Illinois.

EBF—Encyclopedia Britannica Films, Inc., 450 W. 56 St., New York 19.

EPS—Edited Pictures System, Inc., 330 W. 42 St., New York 18.

IndU—Indiana University, Audio-Visual Center. Bloomington, Indiana.

Linde—Linde Air Products Company, 30 E. 42 St., New York 17.

McG-H—McGraw-Hill Book Co., Inc., Text-Film Department, 330 W. 42 St., New York 18.

Rolab—Rolab Photo-Science Laboratories, Sandy Hook, Connecticut.

Upjohn—Upjohn Co., Kalamazoo, Michigan.

USOE—U.S. Office of Education, Washington 25, D.C.

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